



Review paper

Carbonation of limestone powder concrete: state-of-the-art overviewMatija Marinković^{*1)}, Andrija Radović²⁾, Vedran Carević¹⁾¹⁾ University of Belgrade, Faculty of Civil Engineering, Bulevar kralja Aleksandra 73, 11000 Belgrade, Serbia²⁾ University of Priština in Kosovska Mitrovica, Faculty of Technical Sciences, Knjaza Miloša 7, 38220, Kosovska Mitrovica, Serbia*Article history*

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*Keywords*concrete,
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Recently, research into finding long-term solutions to CO₂ mitigation in the cement and concrete sectors was initiated since commonly used supplementary cementitious materials are not globally available in sufficient amounts. One of the possible solutions to that problem is to develop concrete with a higher percentage of limestone in the powder phase. This work presents a critical overview of the state-of-the-art in the field of the carbonation resistance of limestone powder concrete. Experimental research performed so far has shown that if the simple replacement of cement with limestone powder is applied in the standard mix design, a maximum of 10-15% of cement (clinker) could be replaced to maintain similar carbonation resistance. It has also been proven that the dilution effect of weakly inert limestone powder can be compensated for with several measures in the mix design of concrete. By adjusting the cement, limestone, and water content and their particle size distribution, it is feasible to design concrete formulations with up to 50% limestone in the powder phase that are comparable to referent Portland cement concrete in terms of rheological and mechanical performance and carbonation resistance. This is an environmentally significant reduction in the clinker content, but it comes at the cost of a larger superplasticizer content. Prediction models for the carbonation resistance of the limestone powder concrete are poorly developed. Amongst them, the *fib* MC 2010 prediction model is considered relatively simple and robust; however, it has not yet been proven that the model is applicable to concrete with a higher content of limestone powder (>15-20% of the powder phase). The future research should be oriented towards further optimization of the concrete mix design and implementing this model on the middle- and high-content limestone concrete carbonation.

1 Introduction

Concrete is the most widely used construction material today. The global production of concrete is extremely high – roughly 33 billion tons of concrete are produced globally each year, or over 4.7 tons per person annually [1]. Humanity ‘consumes’ only water, more than concrete. No alternative to concrete as a major global construction material currently exists that can be applied at sufficient scale. Other materials can be substituted in some applications, but not for such broad applications as current concrete use.

The production of concrete is responsible for 8-9% of global anthropogenic greenhouse gas (GHG) emissions [2]. Cement, aggregates, water, mineral, and chemical admixtures are used to manufacture concrete. Cement (clinker) is, however, the primary driver of GHG emissions from concrete production: emissions from cement production make up 90-95% of total GHG emissions from concrete production [2, 3]. Decarbonization of the sector is therefore an important part of the CO₂ mitigation pathways towards global temperature rise targets.

The obvious solution to this problem is to reduce the amount of clinker in the cement that is used in concrete production and other applications. To do so, part of the

clinker is usually replaced by so-called supplementary cementitious materials (SCMs) with low embodied CO₂. The most common SCMs are reactive by-products (wastes) from other industries or inert minerals, such as:

- fly ash (FA), the residue of the coal combustion in power plants, which has pozzolanic properties if finely ground – in the presence of water reacts with calcium hydroxide to form compounds possessing cementitious properties,
- ground granulated blast furnace slag (GGBS), a by-product of iron and steel production in blast furnaces, which has latent hydraulic activity – reacts with water to form calcium silicate hydrates (C-S-H),
- fillers, inert or weakly reactive fine particulate materials, the most commonly used is limestone powder.

The clinker content in concrete can also be reduced by particle packing mix design methods [4, 5, 6]. The idea is to minimize the void space to be filled with cement paste by selecting appropriate amounts of aggregate of different particle sizes in order to optimize packing. These methods enable better concrete properties with a smaller amount of cement paste.

^{*} Corresponding author:E-mail address: matija.marinkovic.1@gmail.com

Generally speaking, reactive SCMs like GGBS and FA have a lesser impact on the concrete's mechanical and durability-related properties compared to inert or weakly reactive mineral admixtures such as limestone powder [7–10]. This is a consequence of their pozzolanic or latent hydraulic activity, which enables them to have not only the filler effect but also a binder role in the concrete mix. Therefore, a larger part of the clinker can be replaced with reactive SCMs without significantly jeopardizing the concrete's performance at both the material and structural levels. In other words, they are more efficient in reducing the clinker content in the concrete mix if no other measure in concrete mix design or technology is undertaken.

However, due to the high global production of concrete, long-term solutions for CO₂ mitigation require that alternatives for clinker replacement be abundantly available everywhere in the world. According to an UN report [11], there is not much future in replacing clinker with common SCMs such as GGBS and FA because of their limited global availability. The estimate is that quality sources of GGBS and FA will be limited globally to only about 15–25% of cement production by 2050 and are unlikely to increase. This amount is hardly enough for the production of composite cement (CEM II), which contains up to 35% SCMs and is highly utilized in structural concrete. For that reason, alternative SCM systems that use calcined clays, ground limestone, or other minerals and their combinations should be developed, along with particle packing mix design methods. Since minerals are available everywhere in practically unlimited quantities and many of them can be used for such purposes, this could be a more permanent solution to CO₂ mitigation problems in all cement-based building and construction materials. To pursue that direction, it is necessary to explore and develop possible measures to overcome the negative

dilution effect of inert mineral admixtures in concrete, i.e., to increase their efficiency as SCMs.

The objective of this work is to systemize and critically analyze the research performed in the field of concrete with middle-to-high limestone powder content, specifically research regarding the carbonation resistance of such concretes. Based on this critical review, directions for future research in the area are pointed out.

2 Current standards and applications

The use of limestone as a partial replacement for clinker was introduced into cement standards during the 1980s mostly for economic reasons. Currently, most national and international standards allow a certain amount of limestone in the limited range of cement compositions shown in Figure 1 [12]. For instance, the European EN 197-1 cement standard [13] allows up to 35% of limestone substitution in cements within CEM II type. These are CEM II/A (< 20% of limestone) and CEM II/B (between 20% and 35% limestone). Depending on the total organic carbon content (TOC) they are classified as L (TOC < 0.5% of the weight of limestone) and LL type (TOC < 0.2% of the weight of limestone) [14]. Limestone is introduced into cement by grinding it together with clinker, which normally results in cements with a lower strength class than the original pure clinker cement, despite the limited reaction of limestone powder. Therefore, CEM II/B cements typically belong to the lowest-grade strength class (32.5 MPa), while CEM II/A is mostly of the 42.5 MPa class.

The actual application of limestone in cement is significantly lower than the allowable limits in the standards. According to the statistics given in WBCSD [15], the average limestone amount in cement is globally below 7%, and that has been observed only in the last decade (Figure 2).

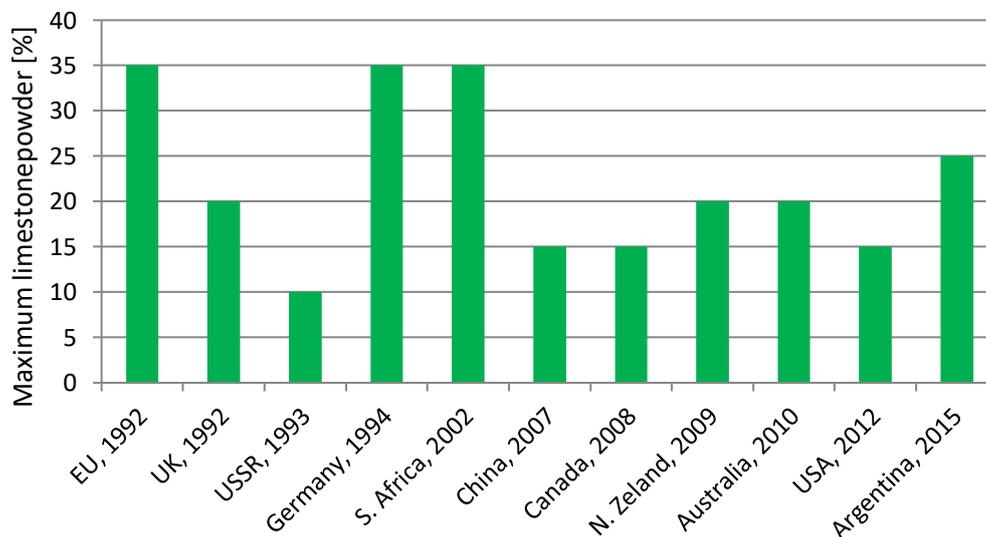


Figure 1. Maximum limestone powder (%) in cements according to standards (figures present the year of the first publication of the standard), adapted from [12]

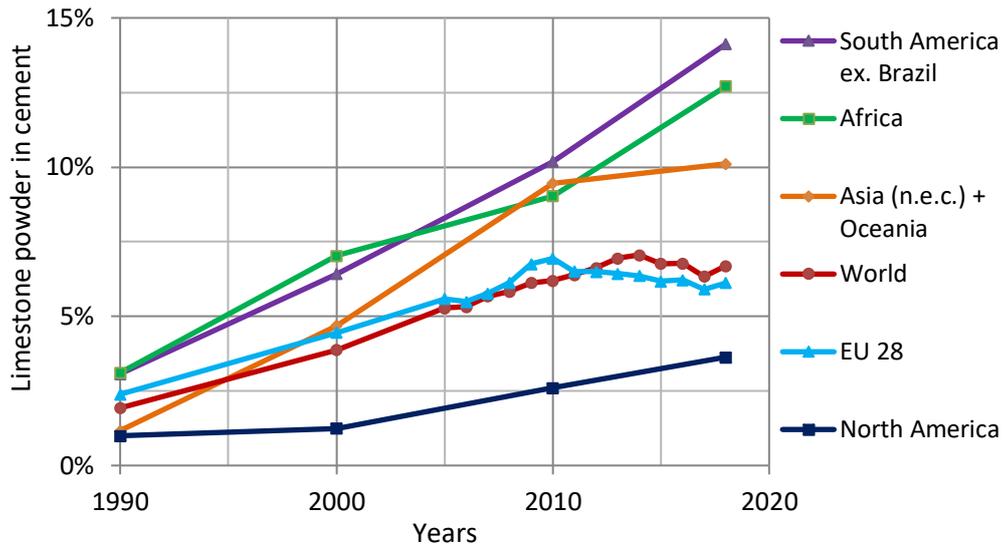


Figure 2. Limestone powder content in cement, data from WBCSD [15]

3 Effects of limestone powder in concrete

Binder is defined as a mineral that hydrates. In modern limestone cements, the clinker part represents the binder. Limestone powder, on the other hand, is almost inert – it partially reacts with aluminates, producing carbo-aluminate and carbo-silicate hydrates [12]. This reaction is weak and produces a low volume of hydrates, meaning that limestone powder physically dilutes the binder phase in concrete. This physical dilution of the binder is the major effect of substituting clinker with limestone powder. It results in a higher porosity of the binder paste and consequently leads to a lower quality of concrete regarding mechanical and durability-related properties that are directly connected to porosity, such as resistance to carbonation, for instance.

Secondly, higher early-age strength is obtained due to an increase in cement hydration rate as a combined effect of dilution and nucleation - the formation of nucleation sites in hydrating cement particles [16]. Besides, early production of carbo-aluminates contributes to the strength of concrete. However, this effect is lost with time – later strength is reduced due to the dilution effect.

Finally, improved particle packing is attainable due to the filler effect of the limestone powder. Finer limestone powder can fill the space between cement particles and improve the packing density of the paste and the interfacial transition zone (ITZ) between paste and aggregates [7]. The magnitude of all these effects depends on the content, fineness, and morphology of the limestone powder.

Currently, several strategies to compensate for the dilution effect of limestone powder are being investigated:

- optimizing the composition of the paste and lowering the water content,
- paste replacement instead of cement replacement,
- particle packing improving, both at the paste and the whole mix (including aggregates) level.

The first is the most efficient one; however, it causes problems with the rheological behavior of concrete. Reduced water content reduces porosity but also reduces the workability of concrete. The second one is based on the function that cement paste has in filling the voids between the aggregate particles. The paste volume must be sufficient

to fill up the voids; otherwise, air will be entrapped in the concrete mix, causing reductions in strength and durability. So the idea is that by adding the limestone powder, the cement paste volume can be reduced by an amount equal to the limestone powder volume while maintaining the total “powder” paste volume needed to fill up the voids. This is equivalent to adding limestone powder to replace an equal volume of cement paste [17]. According to authors [17], such addition of limestone powder as a cement paste replacement without changing the mix proportions of the cement paste should have no adverse effect on the concrete properties but would reduce the cement clinker consumption. Finally, methods to improve particle packing are, in one way or another, included in the previously mentioned strategies.

Therefore, the major research challenge in low-cement (clinker) concrete mix design is how to combine these measures to obtain the maximum possible compensation for the dilution effect while providing the required rheological behaviour. Since the water content required for adequate workability is usually above the content needed for full clinker hydration, the key strategy to improve the performance of low-cement concrete is to keep this excess water to a minimum. In order to obtain this goal, the composition of the paste is optimized regarding the content of water and the content and particle size distribution of clinker and limestone (Figure 3).

According to John et al. [12], the proper combination of a ‘dilution powder’ that has approximately the same particle size as the clinker, an ‘ultra-fine powder’ that reduces the interparticle volume of pores, and a superplasticizer that prevents particle agglomeration to disrupt mobility allows for a significant reduction in water content compared to standard mixtures, as experimentally proved in [18]. An additional reduction in cement content can be realized based on the optimization of aggregate grading and in the increase in total volume of the “powder” paste [17]. However, increasing packing density usually requires more mixing energy. On the other hand, the type and amount of superplasticizer must be chosen carefully to prevent problems with its stability over time and possible retardation of hydration.

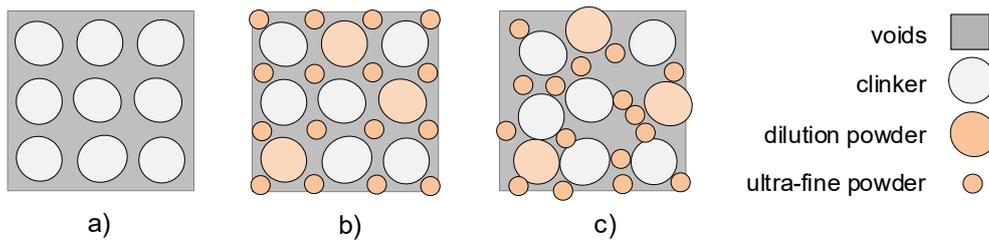


Figure 3. Optimization of the paste composition: a) clinker particles only – high porosity; b) clinker is partially replaced with ‘dilution’ and ‘ultra-fine’ powder and superplasticizer added – improved packing, lower porosity, and lower water demand, and c) without superplasticizer, agglomeration disrupts mobility and destroys packing – higher water demand, adapted from [12]

3.1 Effect on the carbonation resistance of concrete

The calcination process, necessary in cement production, is a chemical reaction in which limestone (which mainly contains calcium carbonate) is converted to calcium oxide and carbon dioxide at high temperatures ($\text{CaCO}_3 + \text{heat} \rightarrow \text{CaO} + \text{CO}_2$). When exposed to air, concrete structures will over time reabsorb CO_2 from the atmosphere in a process called carbonation. It is a physicochemical reaction reversed to calcination in which atmospheric CO_2 diffuses into concrete to react with hydration products (calcium hydroxide and other calcium-rich hydrated oxides) and form calcium carbonate again ($\text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$). For this reaction to happen, it is necessary that CO_2 be dissolved in the pore solution. Carbonation causes a reduction in the alkalinity of the pore solution in the concrete (mainly because of the loss of Ca(OH)_2). However, a highly alkaline environment inside concrete is essential to form the passive film of ferrous oxide at the surface of steel reinforcement, protecting steel from active corrosion. When the carbonation front propagates, the initially formed passive film is gradually destroyed, and consequently, the steel reinforcement becomes more vulnerable to electrochemical corrosion in the presence of moisture and oxygen. On the other hand, carbonation decreases to a certain extent the total porosity due to the precipitation of CaCO_3 on the pore walls, slowing down the carbonation process in that way. Carbonation is generally considered one of the major causes of the deterioration of reinforced concrete structures. Jones et al. [19] state that 2/3 of all structural concrete is exposed to environmental conditions that favour carbonation-induced corrosion.

Since carbonation is a diffusion-controlled process, the relationship between the carbonation depth d_c and time t can generally be described as $d_c = k \cdot \sqrt{t}$. The carbonation rate coefficient k is directly proportional to mass transport properties or the permeability (p), which is related to the porosity of the concrete (total volume of the pores, their size, and interconnectivity), and it is inversely proportional to the alkaline reserve (a):

$$k \propto \frac{p}{a} \quad (1)$$

The alkaline reserve depends on the chemical composition and the number of hydrated phases. Therefore, if cement is replaced with limestone while holding all other variables constant, the carbonation rate coefficient k increases (carbonation is accelerated) because a decreases. The content of Ca(OH)_2 is reduced by dilution of limestone, leading to less carbonatable constituents for carbonation reactions in a low-cement paste [8]. In addition, highly porous mixtures allow faster diffusion of CO_2 . The

dilution effect is somewhat compensated by the filler and nucleation effects of the limestone powder [20].

The chance to keep the carbonation rate similar to that of concrete with only clinker paste is to reduce the permeability of the limestone concrete and reduce the effective diffusivity of CO_2 in that way. The permeability generally depends on the porosity of hardened cement paste and the proportion and density of ITZ, i.e., mainly on the quality and volume of the paste and the separation between particles. By adjusting the cement, limestone, and water content and their particle size distribution, it should be feasible to design concrete formulations that comply not only with rheological and mechanical performance specifications but also with the required carbonation resistance.

4 Experimental results on the carbonation of limestone powder concrete

In a large part of previous research, the effect of limestone powder on the concrete properties was investigated on concrete made with limestone CEMII/A and CEMII/B cements and keeping the same water content as in the referent pure clinker (Portland cement) concrete [21, 22]. Therefore, concrete mixes contained up to 35% of fine limestone powder as a cement replacement. Since limestone is far easier to grind than clinker, joint grinding produces limestone particles that are finer than clinker particles. It was shown, however, in the previous research that this increased fineness of the limestone powder compared to the clinker fineness, is not efficient enough if the intention is to significantly reduce the clinker content in concrete.

Different authors used different terms for the ratio between the content of water and the content of cement (clinker) + limestone powder. In this text, the original terms (as reported in reviewed articles) are used, and an exact explanation of these terms is given in each case of the presented experimental campaigns.

Elgalhud et al. [21] in their recent study have analysed a large number of experimental results on carbonation of concrete made with Portland-limestone cement, where the vast majority of results were obtained on concretes made with limestone CEMII/A (6-20% of limestone) and CEMII/B cements (21-35% of limestone). Analyzed test results point to the conclusion that replacement of clinker with limestone powder significantly increased the carbonation depth of concrete; the higher the replacement percentage, the greater the increase. Under natural exposure conditions, for 35% limestone powder content, and at equal strength of limestone and pure clinker cement concrete, an average increase of 32% was calculated. In the same case, but at an equal water-to-cement ratio (where cement is understood as cement+limestone) an average increase of 75% was

reported. They have also reported from analyzed test results that accelerated carbonation gave rise to higher carbonation compared with natural exposure: up to 58% on an equal concrete strength basis and 85% on an equal water-to-cement ratio basis. The commonly used accelerated exposure in tests consisted of a CO₂ concentration of up to 5%, a duration of less than 30 days, a temperature of 20–30°C, and a humidity of 61–80%, whereas the natural indoor exposure had a duration of up to 5 years.

Lollini et al. [23] investigated the effect of the percentage of replacement of Portland cement CEM I 52.5 with ground limestone, the water-to-binder ratio, and the cement content on the carbonation resistance. They have experimentally tested concrete mixes with 0, 15, and 30% replacement of Portland cement with limestone powder, three different water-to-binder ratios (binder understood as cement+limestone) equal to 0.61, 0.46, and 0.42, and four different binder contents equal to 250, 300, 350, and 400 kg/m³ of concrete. Besides, the effect of curing time (1, 7, and 28 days) was also investigated. The median particle size (i.e., the particle sizes corresponding to 50% cumulative passing) of about 7.5 µm for both Portland cement and limestone was reported, indicating similar fineness, although the Blaine surface area was 534 m²/kg and 610 m²/kg for Portland cement and limestone powder, respectively. The carbonation resistance was tested on 100 mm cube specimens under accelerated conditions: 20°C, 65% RH (relative humidity), and a 2% CO₂ for different times of exposure. The minimum and maximum carbonation depths were measured with the phenolphthalein test on 20 mm diameter cores taken perpendicularly to the mould surface, and the average value between the two was determined. The accelerated carbonation coefficient K_{ACC} was evaluated according to the relationship $d_c = K_{ACC} \cdot \sqrt{t}$ where d_c is the average carbonation depth at time t . At 30% replacement, K_{ACC} , i.e., carbonation depth was larger for limestone concrete for all water-to-binder ratios and all binder contents. At 15% replacement, K_{ACC} was similar, slightly higher, or slightly smaller compared to that of Portland cement concrete for all water-to-binder ratios and all binder contents. According to the authors, when concretes with equal compressive strength were compared, they showed the same carbonation resistance regardless of the amount of Portland cement replaced with limestone indicating that, provided the compressive strength requirement is guaranteed, the resistance to carbonation is also achieved. However, it is not clear what results support such a conclusion since for all 30% limestone concrete mixes, compressive strengths lower than the lowest strength of Portland cement concrete were reported.

Khokhar et al. [24] tested two concrete mixtures with 40% and 80% (by volume) replacement of Portland cement CEM I 52.5 with limestone powder, keeping the same water content (same powder paste volume). Blaine values were 405 m²/kg and 397 m²/kg for cement (0/100µm) and limestone powder (0/100µm), respectively. The specimens with dimensions of 7 x 7 x 28.4 cm were stored at 20°C and 50% RH for 18 months under natural conditions, and carbonation depths were assessed with the phenolphthalein test. Compared to reference Portland cement concrete, the concrete incorporating limestone powder showed significantly lower resistance to carbonation - four to eight times larger carbonation depth for 40% and 80% replacement, respectively. According to the authors, a possible reason is the dominating effect of the reduction in calcium hydroxide over pore refinement.

Collepari et al. [25] tested concrete mixtures with 15% and 25% replacement of Portland cement CEM I 52.5 and four different water-to-cementitious ratios equal to 0.4, 0.5, 0.6, and 0.7 (cementitious in this work means cement+limestone). Blaine fineness of cement and limestone powder was 530 m²/kg and 550 m²/kg, respectively. Concretes (shape and size of samples not reported) were exposed to natural conditions at 20°C and 60% RH for a year after 28 days of curing at 20°C and 95% RH. Carbonation depths were assessed with the phenolphthalein test as usual. Similarly to Lollini et al. [23], they obtained that at the same water-to-cementitious ratio, the carbonation depth of limestone concrete was larger compared to Portland cement concrete, the increase being larger with a larger replacement level. At the same compressive strength in the range of 40 – 45 MPa (on a 150 mm cube at 28 days), differences were much smaller. For instance, measured carbonation depths after 360 days were 4.8mm, 4.7mm, and 6.9mm for Portland cement concrete, 15% limestone concrete, and 25% limestone concrete, respectively. However, similar compressive strengths were in fact obtained with similar water-to-cement ratios, and since the water content was practically kept constant, the cement content also had to be similar. In other words, no reduction in cement content was obtained with this methodology if similar carbonation resistance is expected.

Another example of tests performed on Portland cement and limestone concrete mixes with different replacement ratios but constant water content was found in Meddah et al. [26]. The percentage replacement was 15, 25, 35, and 45% (by weight), and for each percentage, the water-to-cement ratio (cement understood as cement+limestone) varied from 0.79 to 0.45. Blaine fineness of Portland cement CEM I 42.5 and limestone powder was 381 m²/kg and 638 m²/kg, respectively. So, in this experiment, limestone powder was significantly finer than clinker. Accelerated carbonation testing was performed on cubes of 100 mm size that were wet cured during the first 28 days. The specimens were then pre-conditioned by drying in the laboratory for 14 days and exposed to 4% CO₂ at 20 ± 2°C and 55 ± 5% RH in the carbonation chamber. The carbonation depths were measured by applying a phenolphthalein test. Measured carbonation depths were reported for water-to-cement ratios equal to 0.52 and 0.65. At a water-to-cement ratio equal to 0.65, carbonation depths varied from 15 mm for Portland cement to 42 mm for 45% limestone concrete. At a water-to-cement ratio equal to 0.52, increase was smaller, and carbonation depths varied from 12 mm for Portland cement to 27 mm for 45% limestone concrete. The larger the replacement percentage, the greater the increase in carbonation depth. For 15% replacement, the increase was relatively small (about 3 mm at 0.52 and about 6 mm at 0.65 water-to-cement ratio), which led these authors (as well as many others) to conclude that 15% replacement of clinker with limestone powder is acceptable regarding carbonation resistance. At any replacement ratio, it was necessary to decrease the water-to-cement ratio to decrease the carbonation depth. If the water content is kept constant, this means that the content of clinker must be increased. Again, it was shown that such a mix design philosophy couldn't reduce the cement (clinker) content in the concrete, so the environmental goal could not be achieved.

It is obvious from the presented experimental results that desirable carbonation resistance cannot be achieved with higher replacement percentages (>15-20% by weight) unless something is changed in the mix design. All the previous experimental work based on the simple

replacement of cement with limestone powder and standard mix design showed that a maximum 10-15% of cement (clinker) could be replaced to maintain similar carbonation resistance [23-27].

As mentioned in Chapter 3, one possible measure is to reduce the water-to-cement (clinker) ratio. This procedure suggests the use of a high-performance superplasticizer. Furthermore, the optimization of the packing density is advantageous. The particle size distribution and the fineness of limestone powder play a key role in that sense. According to Palm et al. [28], parts of the limestone should be ground finer than clinker to serve as nucleation sites and therefore enhance the progress of hydration. Other parts of the limestone should be ground coarser than clinker to provide a broader particle size distribution and, therefore, a better packing density and a lower water demand [28]. This allows the reduction of the water demand and therefore the simultaneous minimization of the clinker content in the cement, as mentioned in Chapter 3.

This strategy of lowering the water-to-cement ratio in concrete mix design was thoroughly investigated and developed by a group of authors at the Technical University in Darmstadt, Germany [18, 28]. Some of their tested concrete mixture proportions and experimental results reported in [18] are presented in Table 1. Exact values of table-test flow were not reported, but it was stated in the article that the target value of table-test flow diameter of 550 mm was fulfilled in all mixtures.

The Blaine value of the limestone powder was 310 m²/kg while this value was not reported for the used Portland cements. Carbonation resistance was tested under accelerated conditions. After 28 days of curing (7 days in water and 21 days at RH 65% and a temperature of 20°C),

concrete samples (prisms 100×100×500 mm) were exposed to 2% CO₂, RH65% and a temperature of 20°C in the carbonation chamber. Carbonation depths were measured using the phenolphthale test.

It can be observed from Table 1 that not only the lowering of the water content was applied in the concrete mix design but also the measure of increasing the total powder paste volume, since the content of applied limestone powder was much larger than the content that corresponded to simple cement replacement. It can also be observed that limestone concretes had similar strength and carbonation resistance to Portland cement concrete with a water-to-cement ratio of 0.75 and a cement content of 240 kg/m³. Although these concretes can be characterized as low-strength concretes, a reduction in clinker content of 37.5% was achieved. This is a significant reduction from an environmental point of view.

The same authors [18] also tested the influence of the limestone powder fineness, with the idea of enabling a further reduction in the water content. So they substituted successively the 'ordinary' limestone powder (limestone 1 in Table 2) with the Blaine value of 310 m²/kg and d₅₀=15.4µm with very fine limestone powder with the Blaine value of 1600 m²/kg and d₅₀=1.8µm (limestone 2 in Table 2).

Substitution of the ordinary with very fine limestone powder from 0-100% resulted in a compressive strength increase from 32 to 46 MPa. However, the lowest concrete viscosity and consequently the lowest demand for superplasticizer were obtained with a replacement ratio of 30%. These tests showed that particle size distribution and the fineness of the powder significantly affect the packing density, workability, and strength of concrete. The carbonation depths of the concrete mixes in Table 2 were not reported.

Table 1. Mixture proportions and measured carbonation depths [18]

concrete	cement kg/m ³	fly ash kg/m ³	limestone kg/m ³	water kg/m ³	aggregate kg/m ³	SP kg/m ³	w/c [*] /	f _c ^{**} , 28 days MPa	d _c mm
CEMI 52.5	270	10	-	165	1890	2.8	0.61	53.9	2.9
CEMI 42.5	270	10	-	165	1896	1.9	0.61	40.8	2.8
CEMI 32.5	270	10	-	165	1896	3.0	0.61	34.7	5.6
CEMI 52.5	240	-	-	180	1887	-	0.75	33.6	6.1
CEMI 32.5	240	-	-	180	1887	1.3	0.75	24.0	11.1
C150L289w145	150 ^{***}	-	289	145	1781	5.1	0.97	27.6	12.3
C150L289w125	150 ^{***}	-	289	125	1829	6.5	0.83	37.8	8.4

* water-to-cement ratio (cement refers to the amount of Portland cement)

** 150 mm cubes

*** CEMI 52.5

Table 2. Effect of the limestone powder fineness [18]

concrete	CEM1 52.5 kg/m ³	limestone 1 kg/m ³	limestone 2 kg/m ³	water kg/m ³	SP kg/m ³	w/c [*] /	f _c ^{**} , 28 days MPa
C150L289/0	150	289	0	142	2.5	0.96	32.0
C150L246/43	150	246	43	142	2.5	0.96	36.8
C150L202/87	150	202	87	142	1.8	0.96	40.3
C150L159/130	150	159	130	142	2.2	0.96	40.1
C150L116/173	150	116	173	142	3.0	0.96	44.2
C150L72/217	150	72	217	142	3.0	0.96	46.3
C150L0/289	150	0	289	142	3.1	0.96	45.7

*) water-to-cement ratio (cement refers to the amount of Portland cement)

**) 150 mm cubes

The effect of particle size distribution and the fineness of the limestone powder was also investigated in Palm et al. [28]. This effect was investigated on concretes with 50% (by weight) replacement of cement (clinker) with three different limestone powders, LL1, LL2-1 and LL2-2 (Table 3). Limestone cement CEMII/A-LL 32.5 was adopted as the referent concrete. The terms cement and designation *c* in the w/c ratio in this work refer to the amount of CEMII/A-LL, and to the amount of cement+limestone in concretes with 50% replacement, respectively (designation of these concretes is CEM in Table 3).

Blaine values of limestone powders were: 420 kg/m² for LL1, 1050 kg/m² for LL2-1 and 270 kg/m² for LL2-2. The Blaine value of CEMII/A-LL was 365 kg/m². It should also be noted that the clinker part in CEM concretes was in fact CEMI 52.5 with a Blaine value of 551 kg/m². Each tested concrete mix was prepared with only one type of limestone powder.

Carbonation resistance was tested on 100×100×500 mm prisms under accelerated conditions: (2%CO₂, temperature equal to 20 ± 2°C and RH equal to 65 ± 5%) for 28 days. Before testing in the carbonation chamber, concrete samples were cured for 6 days in water and for 21 days at a RH of 65% and a temperature of 20°C. Carbonation depths were measured using the phenolphthalein test.

Let us choose CEMII/A-LL 32.5 with w/c equal to 0.5 as a reference middle-strength concrete with reasonably good carbonation resistance. It can be seen from Table 3 that concrete with 50% clinker replaced with limestone powder LL1 and w/c equal to 0.45 has significantly lower compressive strength and carbonation resistance. However, if the w/c is reduced to 0.35, all concretes with 50% limestone powder, regardless of the limestone type, have comparable or even higher strength and resistance to carbonation. The clinker part in CEMII/A-LL 32.5 ranges between 80 and 94%, in this case between 256 and 300 kg/m³. Since the clinker part in CEM concretes with w/c equal to 0.35 was equal to 190 kg/m³, the reduction in clinker content ranges between 25 and 37%, which is important from an environmental point of view. The cost is a significantly higher amount of superplasticizer: 2.6-11.9 kg/m³, depending on the limestone powder fineness, instead of 1.6 kg/m³.

Zhang et al. [7] have also experimentally shown that this approach in the mix design - lowering the water content – can have a positive effect on the carbonation resistance of limestone concrete, as well as on other properties. They tested two concrete mixes with the same amount of Portland cement CEM I 42.5 (240 kg/m³) and limestone powder (160 kg/m³) but different water contents equal to 160 kg/m³ and 136 kg/m³. Therefore, the replacement percentage was 40% in both mixes, while the water-to-binder ratios were equal to

0.4 and 0.33, respectively (binder is understood as cement+limestone). Since the water-to-binder ratios were low, relatively high amounts of superplasticizer were applied (6.36 and 8.18 kg/m³, respectively), although measured slumps were not reported. Actual Blaine fineness was also not reported, but from the figure showing the particle size distribution, it can be concluded that limestone powder was significantly finer than cement. The carbonation tests on 100 mm cubes (after 3 and 28 days of standard curing) were conducted with a constant temperature and humidity (20±1°C, 60%±10% RH) in natural conditions for 1 year. For both periods of curing, measured carbonation depths were significantly lower for the mix with lower water content, i.e., a lower water-to-cement ratio: at 3 days of curing, carbonation depths were 9.8 mm and 6.7 mm, and at 28 days of curing, 4.5 mm and 2.7 mm for the mix with higher and lower water content, respectively. Since the total (cement and limestone) powder content was the same in both mixes, lower water content resulted in a lower water-to-cement ratio, which resulted in lower porosity and permeability of the concrete. No reference concrete with Portland cement was tested.

The strategy of “paste replacement”, promoted by Chen et al. [17], is presented in the following text, although the authors did not investigate the carbonation resistance itself but compressive strength, water permeability, and sorptivity, as well as permeable porosity. However, these concrete properties are connected to carbonation resistance and therefore can indicate the effectiveness of this strategy. The authors tested three groups of concrete mixtures in which the volume of limestone powder was 0, 4, or 8% of the concrete volume. Within each group, three water-to-cement ratios (the term cement refers to the amount of used Portland cement, CEM I 52.5) were tested: 0.4, 0.5, and 0.6. In all concrete mixtures, the powder paste volume (cement paste + limestone powder), expressed as a percentage of the concrete volume, was kept constant at 34%. The mean particle sizes (d₅₀) of Portland cement and limestone powder were equal to 11.4 μm and 14.5 μm, respectively (similar fineness).

Mixture proportions and some of the experimental results are presented in Table 4. From these results, it can be concluded that the addition of limestone powder as a cement paste replacement, at a constant water-to-cement ratio increased the compressive strength and reduced the water penetration depth and permeable porosity. According to the authors, this indicated that the added limestone powder, which had a similar fineness as cement, was capable of filling into pores in concrete to reduce the porosity. The cost is, as before, the larger required amount of superplasticizer, which was almost doubled for the 8% addition of limestone powder.

Table 3. Mixture proportions and measured carbonation depths [28]

concrete	cement* kg/m ³	w/c /	SP kg/m ³	table flow mm	f _c ** ₂₈ days MPa	d _c mm
CEMII/A-LL 32.5	280	0.6	0	485	26.3	8.9
CEMII/A-LL 32.5	320	0.5	1.6	565	38.8	6.3
CEM(50% LL1)	335	0.45	NA	NA	26.7	11.5
CEM(50% LL1)	380	0.35	2.6	620	49.1	6.3
CEM(50% LL2-1)	380	0.35	5.7	515	52.1	3.9
CEM(50% LL2-2)	380	0.35	11.9	550	36.8	6.1

*) amount of CEMII/A in CEMII concretes, and amount of CEMI 52.5+limestone powder in CEM concretes

**) 150x300mm cylinder

Table 4. Mixture proportions and experimental results [17]

	cement	limestone powder	water	cement paste, vol.	SP, by mass of powder	slump	f_c^{**}	Penetration depth	Permeable porosity ^{***}
concrete	kg/m ³	kg/m ³	kg/m ³	%	%	mm	MPa	mm	%
C-0.4-0 [*]	470	0	188	34	0.98	225	74.8	31.0	10.1
C-0.4-4	415	106	166	30	1.23	245	80.5	19.5	8.4
C-0.4-8	359	211	144	26	1.94	255	85.1	18.5	7.8
C-0.5-0	413	0	207	34	0.89	230	56.0	56.0	14.3
C-0.5-4	364	106	182	30	0.98	235	62.0	26.5	10.4
C-0.5-8	315	211	158	26	1.57	255	68.7	23.0	8.8
C-0.6-0	368	0	221	34	0.48	210	44.3	75.0	16.2
C-0.6-4	325	106	195	30	0.79	230	49.2	36.0	12.5
C-0.6-8	281	211	169	26	1.05	230	51.5	29.0	10.9

^{*}) C-w/c-%of limestone powder

^{**}) 150 mm cubes at 28 days

^{***}) the volume of pores that can be filled by water, expressed as a percentage of the concrete volume

Figure 4 presents the relationship between the carbonation depth and mean compressive strength of concrete, for Portland cement concrete (OPC) and limestone powder concrete (LS) with 15-65% (by weight) of limestone in the powder phase, calculated on a larger database. In total, 45 experimental results on the carbonation depth measured under accelerated conditions were taken from [18, 23, 25, 26, 28-32]. Since the concentration of CO₂ and the exposure time were different in the analysed research, the results on measured carbonation depth were converted to a CO₂ concentration equal to 2% and an exposure time equal to 28 days. As already mentioned in Chapter 3.1, the carbonation process can generally be described with the following equation:

$$d_c = k \cdot \sqrt{t} = K \cdot \sqrt{CO_2} \cdot \sqrt{t} \quad (2)$$

where carbonation rate coefficient k can be expressed as $K \cdot \sqrt{CO_2}$, K being a coefficient that depends on the concrete properties, curing, and environmental conditions, and CO_2 being a concentration of CO₂ in %. Considering the fact that

the coefficient K does not depend on the CO₂ concentration, the previous equation allows us to compare the two carbonation depths ($d_{c,1}$ and $d_{c,2}$) from different test conditions (CO₂ concentrations ($[CO_2]_1$ and $[CO_2]_2$) and exposure times (t_1 and t_2)) for the same concrete type in the form:

$$\frac{d_{c,1}}{d_{c,2}} = \frac{\sqrt{[CO_2]_1}}{\sqrt{[CO_2]_2}} \cdot \frac{\sqrt{t_1}}{\sqrt{t_2}} \quad (3)$$

For $[CO_2]_1 = 2\%$ and $t_1 = 28$ days, it follows:

$$d_{c,1} = d_{c,2} \cdot \frac{\sqrt{2}}{\sqrt{[CO_2]_2}} \cdot \frac{\sqrt{28}}{\sqrt{t_2}} \quad (4)$$

Reported compressive strengths of concrete were converted to the strength of a 150 mm cube and were considered as the mean compressive strength f_{cm} .

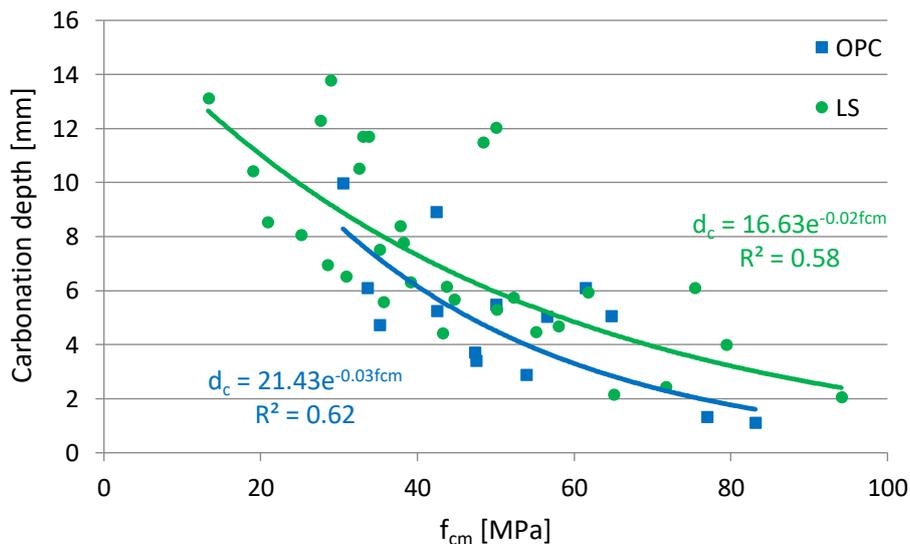


Figure 4. Relationship between the carbonation depth and mean compressive strength of concrete for Portland cement concrete (OPC) and limestone powder concrete (LS) with 15-65% (by weight) limestone in the powder phase

Figure 4 shows, as expected, that limestone powder concrete has a lower resistance to carbonation compared to OPC concrete. Experimental results were best fitted with exponential functions; however, the scatter is large for both types of concrete. In order to find out whether there is a limit in the limestone content where carbonation resistance similar to that of the OPC can be expected, the limestone concretes were divided into 3 groups with different limestone contents, as shown in Figure 5.

If we compare the carbonation depth of analyzed concrete mixes at equal strength, concrete with 15-25% limestone powder in the total powder phase performed even better than Portland cement concrete. With increasing limestone content, the resistance to carbonation decreased. Concrete with 26-35% limestone powder in the total powder phase had slightly lower carbonation resistance, while concrete with 45-65% limestone powder in the total powder phase showed significantly lower carbonation resistance; carbonation depth was on average doubled compared to Portland cement and 15-25% limestone concrete. Again, the experimental results were best fitted with exponential functions. It should be kept in mind that these relationships were obtained from a limited amount of experimental data, which may be the reason for the relatively high scatter of results. What is interesting, however, is that the scatter obtained for Portland cement concrete was higher than the scatter obtained for 15-25% and 26-35% limestone concrete. It can also be observed from Figure 5 that the results obtained by Palm et al. [28] are more of an exception than a general rule, pointing to a need for further experimental investigation into concrete mix design optimization.

5 Prediction models

The basic factors that influence the carbonation of cementitious materials are mixture proportions and related material quality, stress state (whether compression or tension [33], existence of cracks [34, 35]), environmental exposure (relative humidity, temperature, concentration of

CO₂, and eventual coupling with other exposures such as chloride ingress [36]), and curing conditions.

Generally, mathematical models of the carbonation process are established by understanding the basic influential factors and quantitatively correlating these parameters with carbonation depth. Essentially, these are empirical models, and the vast majority of them are based on Fick's first law: the carbonation process is considered a diffusion of CO₂ through capillary pores under a concentration gradient (2):

$$d_c = k \cdot \sqrt{t} \tag{5}$$

The kinetics of carbonation, however, also depend on the kinetics of the hydration process and pore structure modification over time, which are mostly related to the type of SCM. Some researchers therefore proposed a value of exponent *n* different from 0.5 in the equation (2), modifying the relationship between *d_c* and time while keeping the carbonation rate coefficient *k* constant [37, 38]:

$$d_c = k \cdot t^n \tag{6}$$

So far, many prediction models of different complexity have been developed for Portland cement concrete and concrete with blended cements with FA and GGBS [39] or recycled aggregate concrete [37]. These models do not take into account other deterioration processes that can act simultaneously with carbonation or the effects of stress states and cracks. However, only a few models that can be applied to the concrete with limestone powder were found in the literature.

Wang [40] developed the hydration model that includes the dilution effect and the nucleation effect of limestone powder during the hydration of cement. From this model, he was able to calculate the carbonatable material contents and porosity, and considering the environmental conditions, the CO₂ diffusivity and carbonation depth of concrete. Starting from this model and the model proposed by Papadakis [41], Wang recently [16] proposed the following model for the carbonation depth of concrete with limestone powder:

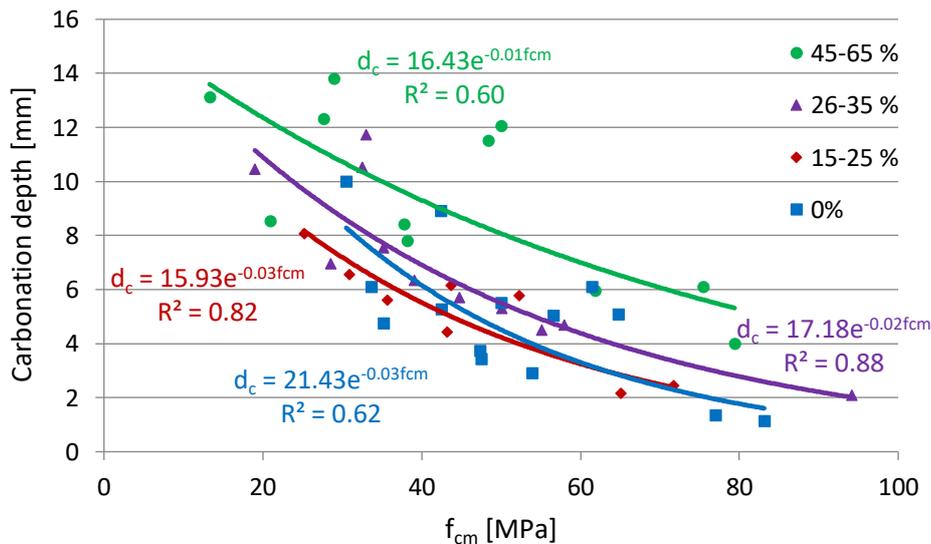


Figure 5. Relationship between the carbonation depth and mean compressive strength of concrete for Portland cement concrete (0%) and limestone powder concrete with different percentages of limestone in the powder phase

$$d_c = \sqrt{\frac{2D \cdot (CO_2)}{0.33 \cdot CH + 0.214 \cdot CSH}} \cdot \sqrt{t} \quad (7)$$

where

- d_c is the carbonation depth
- D is the CO_2 diffusivity
- (CO_2) is the concentration of CO_2 in the exposure environment
- CH is the mass of calcium hydroxide hydrate
- CSH is the mass of calcium silicate hydrate

The CO_2 diffusivity depends on the concrete porosity and exposure conditions and author purposed the following equation:

$$D = 6.1 \cdot 10^{-6} \cdot \left(\frac{\varepsilon}{\frac{C}{\rho_C} + \frac{LS}{\rho_{LS}} + \frac{W}{\rho_W}} \right)^3 \quad (8)$$

$$\cdot (1 - RH)^{2.2} \cdot \exp \left[\beta \left(\frac{1}{T_{ref}} - \frac{1}{T} \right) \right]$$

where

$$\varepsilon = \frac{W}{\rho_W} - \frac{0.25 \cdot C \cdot \alpha}{\rho_{CW}} - \frac{1.62 \cdot LS \cdot \alpha_{LS}}{\rho_{CW}} - \Delta \varepsilon_C \quad (9)$$

is the porosity of carbonated concrete

- $W, C,$ and LS are the contents of water, cement and limestone powder, respectively
- $\rho_C, \rho_{LS}, \rho_W,$ and ρ_{CW} are the densities of cement, limestone powder, mixing water, and chemical combined water, respectively
- α, α_{LS} are the degrees of the reactions of cement and limestone powder, respectively
- RH is the relative humidity of the environment
- $\beta = 4270$ is the activation energy of the CO_2 diffusion
- $T_{ref} = 293K$ is the reference temperature
- T is the environmental temperature

The equations for the calculation of the amounts of carbonatable compounds, CH and CSH, and degrees of cement and limestone powder reactions, α and α_{LS} were provided in the paper [16]. This rather complex model takes into account the reduction of concrete porosity due to the hydration of cement, the reaction of limestone powder, and carbonation (second, third, and fourth terms in equation (9), respectively). The reduction due to carbonation $\Delta \varepsilon_C$ can be evaluated using the change in the solid volume of reactants and products of carbonation [41]. The model was tested on limestone concretes with a 10% and 20% replacement ratio, and a good correlation with the experimental results was obtained.

Shah and Bishnoi [8] developed the empirical equation to predict carbonation depth in Portland cement and various blended cement concretes. They used the concrete strength and water-to-cement ratio instead of porosity in computing diffusion coefficient D , arguing that the properties of ITZ also have an impact on carbonation resistance. On the other

hand, their model did not take into account the changes occurring in the microstructure due to carbonation that could alter the diffusion characteristics significantly. The model was tested against the experimental results obtained on several binary and ternary blend compositions (FA, limestone, and two types of clay at 45% joint replacement), and a reasonable correlation was obtained.

Beside Papadakis' models for carbonation of Portland cement and blended cement concrete [42, 41], Yang's model [43] is also often referred to. However, the correction factors for the substitution of cement with SCMs are given for FA, GGBS and silica fume and not for the limestone powder in this model.

It is obvious that such mathematical models are extremely time- and cost-consuming for every-day engineering practice and that simpler models are needed. One such simpler and more robust model, which considers the concrete quality, curing conditions, and environmental conditions, is given in the *fib* Model Code 2010 [44]. The Model Code 2010 equation has already been applied in practice for the assessment of carbonation depth d_c with time t :

$$d_c = k \cdot W(t) \cdot \sqrt{t} \quad (10)$$

where

$$k = \sqrt{2 \cdot k_e \cdot k_c \cdot R_{NAC,0}^{-1} \cdot C_s} \quad (11)$$

is the carbonation rate coefficient

- k_e is the environmental function [-]
- k_c is the execution transfer parameter [-]
- $R_{NAC,0}^{-1}$ is the inverse effective carbonation resistance of concrete under natural conditions [(mm²/years)/(kg/m³)]
- C_s is the CO_2 concentration in the air [kg/m³]
- $W(t)$ weather function [-]

The inverse effective carbonation resistance of concrete under natural conditions $R_{NAC,0}^{-1}$ is a property of concrete that depends mostly on the water-to-cement ratio and binder type. The determination of this concrete property would, however, take years. For that reason, Code purposefully applied the inverse effective carbonation resistance measured under accelerated carbonation conditions $R_{ACC,0}^{-1}$ and established the relationship between them:

$$R_{NAC,0}^{-1} = k_t \cdot R_{ACC,0}^{-1} + \varepsilon_t \quad (12)$$

where

- $R_{ACC,0}^{-1}$ is the inverse effective carbonation resistance of dry concrete, determined at a certain time t_0 using the accelerated carbonation test ACC [(mm²/years)/(kg/m³)]
- $R_{NAC,0}^{-1}$ is the inverse effective carbonation resistance of dry concrete (65%RH) at a certain time t_0 using the normal (natural conditions) carbonation test NAC [(mm²/years)/(kg/m³)]
- k_t is the regression parameter for the test effect of the ACC test [-]
- ε_t is the error term for inaccuracies which occur conditionally when using the ACC test method [(mm²/years)/(kg/m³)]

For further instructions, MC 2010 refers to *fib* Model Code for service life design [45] in which all the required parameters are given. $R_{ACC,0}^{-1}$ is to be determined experimentally and conditions for the ACC test are defined: 100/100/500 mm prisms are to be exposed to CO₂ 2% vol., temperature equal to 20°C and RH equal to 65% for 28 days. If no test data is available, *fib* Model Code for service life design offers $R_{ACC,0}^{-1}$ values for several cement types (CEM I, CEM I+FA and CEM III) and several water-to-cement ratios. So, the model should be valid for all binder types and water-to-cement ratios, only the $R_{ACC,0}^{-1}$ has to be measured.

However, some researchers have proven that for some binder types, for instance, binders with high amounts of FA, this doesn't have to be true [37]. There is, of course, the question of the capability of the ACC tests to represent the real natural conditions. Some researchers have pointed out that the kinetics of carbonation can be significantly changed under accelerated conditions, especially for high (>4%) CO₂ concentrations [37, 46, 47]. Moreover, this effect is different for different types of SCM, probably depending on their different reactivity, whether being inert or having pozzolanic activity. Lollini and Redaelli in their recent study [9] showed, however, that the ACC conditions in [45] were chosen well, at least for the outdoor sheltered conditions. They compared the measured carbonation rate coefficient of concretes with various types of SCM, including concretes with up to 30% limestone powder, under natural (outdoor sheltered for 12 years) and accelerated conditions according to [45] and obtained reasonable agreement. They also concluded that the type of binder had the greatest effect on the quality of the modelling of NAC with ACC conditions.

Although relatively simple, the application of this model requires an experimental determination of $R_{ACC,0}^{-1}$. In that way, this property gets the same importance as the compressive strength of concrete in practical applications: it has to be experimentally determined. Aside from the time needed for the ACC test, proper laboratory equipment (carbonation chamber) is also required. Finding alternatives, for instance, by connecting empirically $R_{ACC,0}^{-1}$ to the compressive strength of concrete, would significantly improve the practicability of the model.

6 Conclusion

From the analysis of the experimental and theoretical work in the area of the carbonation resistance of concrete with limestone powder, the following conclusions are drawn:

- replacing the clinker with up to 15% limestone powder practically does not affect the resistance to carbonation,
- replacing the clinker with a higher content of limestone powder significantly reduces the carbonation resistance, if no other measure in the concrete mix design and technology is undertaken; the decrease is larger with a larger replacement ratio,
- several measures in the concrete mix design were experimentally proven to be effective in compensating the dilution effect of limestone powder: lowering the water content, increasing the powder paste volume, and improving the particle packing by combing the powders with different fineness,
- concrete with 50% of limestone in the powder phase can be designed to have satisfactory carbonation resistance

(in comparison to the pure-clinker concrete), enabling the environmentally significant reduction of clinker; however, this comes at the cost of a significantly larger superplasticizer content,

- several complex mathematical prediction models of the carbonation resistance of limestone concrete, based on Fick's first law, can currently be found in the literature,
- it is not yet proven that the *fib* MC 2010 prediction model is applicable to concrete with a higher content of limestone powder (>15-20% of the powder phase).

The *fib* MC 2010 prediction model for concrete carbonation is relatively simple and robust and therefore recommendable for practical applications. The future research should be oriented towards advancements in mix design optimization and implementing this model on middle- and high-content limestone concrete carbonation. Further, in order to avoid the experimental determination of the ACC inverse effective carbonation resistance, finding the empirical relationship to the compressive strength of concrete would significantly improve the practicability of the model.

In general, research on the new SCMs, such as calcined clay or calcined sand, is recommended. It is necessary to find and investigate long-term solutions to CO₂ mitigation that can replace commonly used FA and GGBS, keeping in mind that these SCMs are not globally available in sufficient amounts.

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