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Report of RILEM TC 281-CCC: A critical review of the standardised testing methods to determine carbonation resistance of concrete

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Abstract The chemical reaction between CO_2 and a blended Portland cement concrete, referred to as carbonation, can lead to reduced performance, particularly when concrete is exposed to elevated levels of CO_2 (i.e., accelerated carbonation conditions). When slight changes in concrete mix designs or testing conditions are adopted, conflicting carbonation results are often reported. The RILEM TC 281-CCC '*Carbonation of Concrete with Supplementary Cementitious Materials*' has conducted a critical analysis of the standardised testing methodologies that are currently applied to determine carbonation resistance of concrete in different regions. There are at least 17 different standards or recommendations being actively used for this purpose, with significant differences in sample curing, pre-conditioning, carbonation exposure conditions, and methods used for determination

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of carbonation depth after exposure. These differences strongly influence the carbonation depths recorded and the carbonation coefficient values calculated. Considering the importance of accurately determining carbonation potential of concrete, not just for predicting their durability performance, but also for determining the amount of CO_2 that concrete can re-absorb during or after its service life, it is imperative to recognise the applicability and limitations of the results obtained from different tests. This will enable researchers and practitioners to adopt the most appropriate testing methodologies to evaluate carbonation resistance, depending on the purpose of the conclusions derived from such testing (e. g. materials selection, service life prediction, CO_2 capture potential).

Keywords Carbonation · Concrete · Supplementary cementitious materials · Standards

1 Introduction

Chemical durability of concrete is often determined according to standardised accelerated testing methods that are intended to simulate the most damaging environmental scenarios that concrete structures will endure during their service life. In many instances such testing protocols are derived from empirical experience and can be far from accurate in simulating the in-service environmental exposure conditions of a given concrete structure. In other cases, the test method specification documents do not provide sufficient details about the procedures to follow, which gives a great degree of freedom to adjust the testing methods, and consequently the results obtained might not be comparable among different studies, or applicable in predicting the long-term performance of concrete. This is of particular concern as novel cement and concrete formulations are being developed to decarbonise the construction sector, and there is a growing acceptance of the need to adopt performance-based standards to enable their use [1]. Often, performance of blended or alternative cementitious materials is tested by following prescriptive standards that have been developed for Portland cement concrete, that do not account for the differences in reaction kinetics, chemistry, and/or microstructure in concrete with supplementary cementitious materials (SCMs). This

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necessitates evaluation of the testing methodologies that are currently used to evaluate chemical durability of modern concretes, to assess their applicability for determining whether a particular concrete will meet the demands of a specified application.

Carbonation is one of the major deterioration mechanisms of concrete structures, and as discussed by von Greve-Dierfeld et al. [2], it can lead to significant changes in the microstructure and performance of concrete containing different SCMs. It is expected that carbonation will occur slowly over several decades during the service life of concrete structures; however, increasing CO_2 concentrations in the air, changes in climate, as well as changes in cementitious binder formulation chemistry affect how rapidly carbonation might occur [3, 4]. Accelerated testing methods are often used to evaluate the resistance of concrete to carbonation during accessible time frames (months rather than years or decades) under controlled exposure conditions. It is well known that the exposure conditions adopted in standards to determine chemical durability of concrete are not representative of all natural environments or climates, but it is in many cases intended that the testing conditions simulate worst-case scenarios. It is thus important to ensure that the accelerated test methods produce results that are relevant in understanding, and hopefully also predicting, how concrete might perform during its service life, and beyond this time if concrete re-carbonation after demolition is considered to be relevant.

The RILEM Technical Committee (TC) 281-CCC conducted two extensive interlaboratory tests with the goal of determining the reproducibility of concrete carbonation rate results when evaluated under different accelerated [5] or natural [5] exposure conditions. For concrete with SCMs tested under accelerated carbonation, it was concluded [5] that conventionally used standardised testing methods or recommendations provide similar carbonation resistance rankings, although the carbonation rate values were significantly different across different exposure environments. Of significance for service life prediction, no correlations between the fresh or hardened properties of concretes and their accelerated carbonation performance were identified. When evaluating similar mortar and/or concrete mixes under natural carbonation exposure conditions [5] similar rankings were also recorded, and the differences associated with climatic

variations tested in this study (e.g. relative humidity/temperature, with shelter/ unsheltered) were deemed statistically insignificant. By using the data collected in these interlaboratory tests, it was investigated whether a direct correlation between accelerated and natural carbonation rates could be drawn for the concrete mixes evaluated. The results revealed that the best correlation is achieved when materials were tested according to existing EN standards (EN 12390-10 and EN 12390-12). The results from this extensive testing campaign further demonstrate the significant impact of the testing methods adopted in the response of concrete when exposed to carbonation.

As early as 1907, in an effort to simulate and predict how concretes could perform during their service life, natural carbonation exposure studies were conducted to investigate the relationship between carbonation and reinforcement corrosion, and those observations underpinned the evolution of accelerated testing exposure conditions that were accepted by industry and development for over a century [7]. Carbonation resistance testing standards have been developed for many decades, as it became evident that carbonation posed a major threat to the concrete-based built environment. Historically, standardisation organisations across the world have developed such standards in close collaboration with different stakeholders with expertise in their subject matter and who know the needs of the organisations or sectors they represent, with the aim to reach a consensus and agree on a way to conduct such tests. One of the earlier recommendations developed as a guideline for carbonation testing of concrete is RILEM CPC 18 '*Measurement of hardened concrete carbonation depth*' [8] from 1988, which underpinned the development of later European standards to determine carbonation resistance of concrete. This recommendation created awareness of the different parameters that needed to be recorded and understood when reporting carbonation results, as they influence the performance of concrete.

1.1 Case study—History of carbonation standards in Japan

In different regions, the development of standards for evaluating carbonation resistance of concrete has taken place over the past decades. As an example, the evolution of standards in Japan is briefly discussed. Nakamura et al. [7] surveyed and

summarised testing conditions and methods adopted in Japan before and after a prescriptive standard was established, comparing such methods with the accelerated carbonation tests from Europe followed at the time (see Fig. 1). For creating the standards, the Japanese Concrete Institute (JCI) organised a Japanese Industrial Standards (JIS) drafting committee in 2001, which promoted the creation of the Japanese Standards Association (JSA) JIS A 1152 '*Method for measuring carbonation depth of concrete*' [9] in 2002 (revised in 2011 and 2018) for evaluating concrete produced in the laboratory or core specimens from existing structures.

In 2003, JIS A 1153 '*Method of accelerated carbonation test for concrete*' [10] was published. This standard was based on ISO 1920-12 '*Determination of the carbonation resistance of concrete — Accelerated carbonation method*'. Both test standards were based on the guidelines prescribed by the Architectural Institute of Japan [1]. In addition to those standards, NDIS 3419 '*Method of test for neutralization depth of concrete in structures with drilling powder*' [11] was approved in 1999 and revised in 2011. Before JIS A 1152 and NDIS 3419 were established, various testing methods were proposed and used to determine carbonation resistance of concrete in Japan.

As illustrated for the case of Japan, empirical evidence and extensive experimental trials motivate changes in prescriptive standards. A given standardised testing methodology that is widely accepted by the construction sector today might have been derived from extensive validation and experimental work for a given set of materials available at the time (e.g. plain Portland cement), which might not be similar to those that will be used in the years to come [12] (e.g. the blended cements currently in widespread use). Therefore, it is imperative to critically assess how durability of concrete is tested, and the limitations of the results obtained from those tests, so that the results can be adequately interpreted in context.

2 Standardised testing methods for determining carbonation resistance of concrete

Several studies have highlighted different existing standardised testing procedures to determine carbonation resistance of concrete, with significant
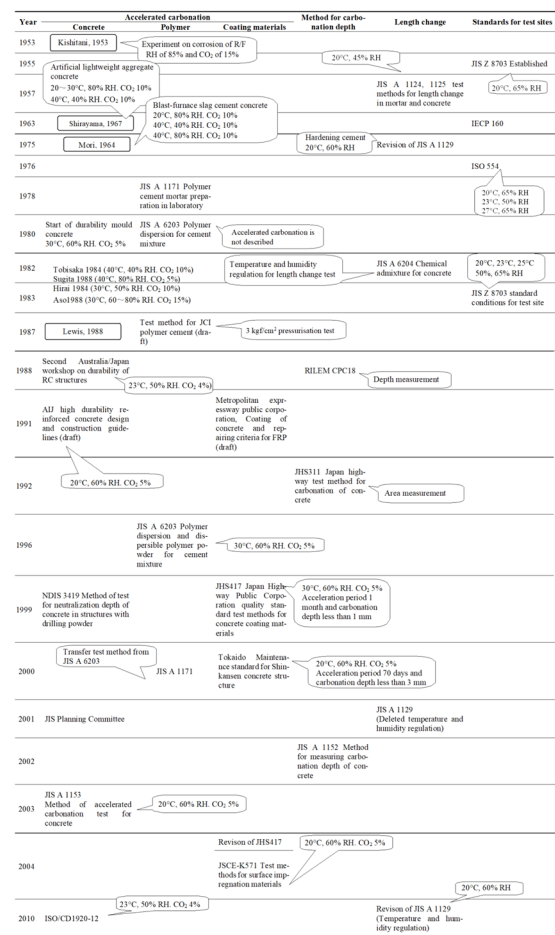
Fig. 1 Evolution of concrete accelerated carbonation tests and other related testing methods in Japan. Some columns indicate the type of material (concrete, polymer, coatings) for which different tests were developed (including accelerated carbonation), as well as the key properties (e.g. method for determining carbonation, length changes) determined with such tests. Adapted from [7]

differences in sample pre-conditioning [13], exposure conditions (CO_2 concentrations, relative humidity), and the method of measurement of carbonation extent (e.g., changes in alkalinity) [14, 15]. A compilation of the existing carbonation standards was created in consultation with the members of RILEM TC 281-CCC and is shown in Table 1.

2.1 Approaches for determining carbonation in regions where no testing methods or standards are defined

Despite the large number of dedicated standards for evaluation of carbonation resistance of cementitious materials (Table 1), there is no ASTM standard for determining carbonation resistance. ASTM standards are some of the most widely used globally for construction materials testing and are often translated

Table 1 Summary of standardised testing methodologies for determining carbonation resistance of concrete, and methods to measure carbonation depth

Geographical scope	Standard ID	Title	References
China	GB T50082-2009	Standard for test methods of long-term performance and durability of ordinary concrete	[16]
Europe	EN 12390-10:2018	Testing hardened concrete. Determination of the carbonation resistance of concrete at atmospheric levels of carbon dioxide	[17]
Europe	EN 12390-12:2020	Testing hardened concrete. Determination of the carbonation resistance of concrete. Accelerated carbonation method	[18]
Europe	EN 13295:2004	Products and systems for the protection and repair of concrete structures. Test methods. Determination of resistance to carbonation	[19]
Europe	EN 14630:2006 *	Products and systems for the protection and repair of concrete structures. Test methods. Determination of carbonation depth in hardened concrete by the phenolphthalein method	[20]
France	XP P18 458:2022	Tests for hardened concrete. Accelerated carbonation test—measurement of the thickness of carbonated concrete	[21]
Global	RILEM CPC-18 (1988)[a]	Measurement of hardened concrete carbonation depth	[8]
Global	ISO 1920-12:2015	Testing of concrete—Part 12: Determination of the carbonation resistance of concrete—Accelerated carbonation method	[22]
Italy	UNI 9944:1992 (withdrawn 2019)	Corrosion and protection of reinforcing steel in concrete. Determination of the carbonation depth and of the chlorides penetration profile in concrete	[23]
India	IS 516 (Part-2/Sec 4) 2021	Hardened Concrete—Methods of Test Part 2 Properties of Hardened Concrete other than Strength Sect. 4: Determination of the carbonation resistance by accelerated carbonation method	[24]
Norway	NT Build 357:1989	Concrete, repairing materials and protective coating—carbonation resistance	[25]
Portugal	LNEC E391:1993	Concrete. Determination of accelerated carbonation	[26]
Spain	UNE 83993-1: 2013	Concrete durability. Testing method. Determining the carbonation penetration rate in hardened concrete. Part 1: Natural method	[27]
Spain	UNE 83993-2: 2013	Durability of concrete. Test method. Measurement of carbonation penetration rate in hardened concrete. Part 2: Accelerated method	[28]
Switzerland	SIA 262/1: 2019	Concrete Structures: Supplementary Specifications	[29]
The Netherlands	CUR-Aanbeveling 48:2010	Procedures, criteria and test methods for testing the suitability of novel cements for application in concrete and for the equivalent performance of concrete with fillers	[30]
United Kingdom	BSI 1881-210:2013	Testing hardened concrete. Determination of the potential carbonation resistance of concrete. Accelerated carbonation method	[31]

[a]Standards that solely indicate how to determine carbonation using a pH indicator

or adapted in different countries for implementation as national standards. This is of particular interest considering that regions such as the American and African continents, which often adopt ASTM standards, are some of the major producers and consumers of concrete, and have a variety of climates in which carbonation-related degradation of concrete may be expected to be significant. Experts based in the United States and Canada have indicated that in the case of North America carbonation, or its potential effect on steel reinforcement corrosion, is not considered a major threat for concrete, as empirical experience from practitioners, up to now, shows that the durability of reinforced concrete structures in that region is mainly compromised by chloride exposure (particularly in coastal areas, or due to use of de-icing salts) before carbonation is identifiable as a notable durability issue. The American Concrete Institute code ACI 318-19 (22) [32] also does not explicitly include provisions related to carbonation. In North America, if carbonation of concrete needs to be tested, the European standards may be followed.

In Africa, there is no consensus across different countries for determining carbonation resistance of concrete, and standards have not been developed for it. When carbonation tests are conducted, they are conducted according to the European or the British Standards. In South Africa, which has a highly developed set of performance-based design protocols for concrete, the oxygen permeability index test may be used to provide information for carbonation rate prediction (among other concrete properties) rather than testing carbonation directly [33]. Africa is rapidly urbanising with increased consumption of concrete, and has regions of high temperature and varying humidity, making the durability challenges associated with carbonation inevitable, in at least some parts of that continent. Thus, there is need to develop an approach to measure carbonation under conditions that are representative of these environments. The RILEM CPC-18 method [8] is cited in some research papers from institutes in Africa, as well as the EN 14630 protocol [20] for determining carbonation depths using the phenolphthalein indicator, but these do not specify the protocols to follow to induce carbonation prior to that analysis.

Australia also does not have a national standard for testing carbonation resistance of concrete. It follows a similar approach to North America where European standards are adopted when this property needs to be tested. In this country the areas of high population density, and consequently concrete structures, are mainly located in coastal areas (Fig. 2), where chloride-induced corrosion is the main threat to the integrity of steel reinforced concrete. Wang et al. [3] simulated the potential effects of climate change on the carbonation of concrete in Australia, and the consequent likelihood of corrosion of steel reinforcement (Fig. 3). With and without considering changes in climate, the structures in regions with highest population density (Fig. 2) will have the lowest probability of carbonation-induced corrosion (Fig. 3); therefore, chloride-induced corrosion, rather than carbonation-induced corrosion, is considered the major practical threat to longevity for the majority of structural concretes in Australia. This explains why perhaps the development of a dedicated standard has not taken place.

In the following sections, the specificities of the standardised testing methods that can influence carbonation results are discussed in detail.

3 Sample specifications, pre-conditioning, and curing age when testing

3.1 Sample geometry and extraction methods

The geometry of the concrete samples used for carbonation experiments varies significantly among different standards (see Table 2). Some recommend the use of cylinders, while others recommend prisms or cubes of different sizes, depending on the number of measurements to be conducted. The shape of concrete samples is also influenced by the source of the concrete specimens to be tested: whether laboratory produced or extracted from real concrete structures. Laboratory concrete samples are often cast in prismatic and/or cubic forms, the latter often being used when a single measurement is being conducted per sample, as the necessary moulds are widely available and used for casting compressive strength testing specimens. Concrete prisms are also recommended in standardised procedures as they allow multiple measurements of the carbonation depth after different periods of carbonation exposure.

In the cast surface of the specimen, accumulation of portlandite is often observed [35], which
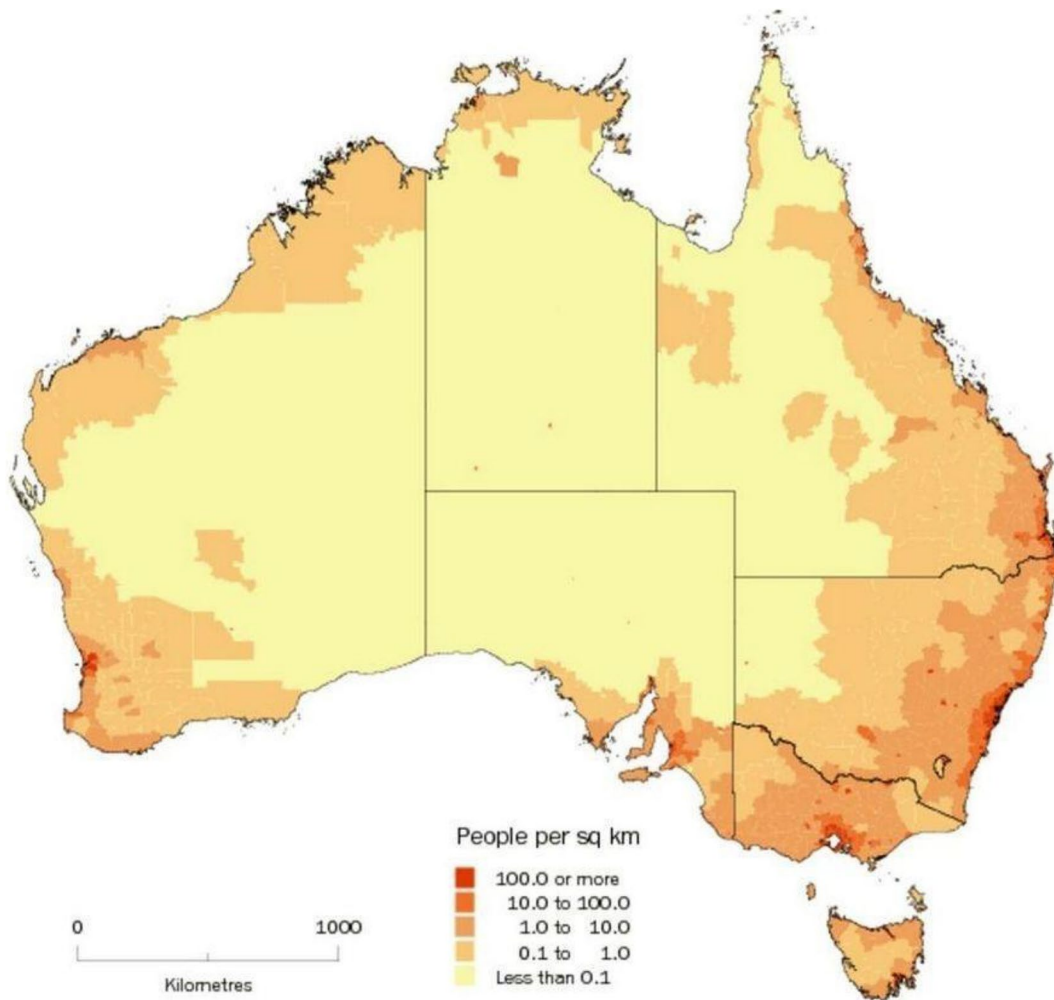
Fig. 2 Population density in Australia. Reproduced from [34], copyright Newebcreations (https://australiamap360.com), used by permission

is expected to influence the measured carbonation depth. The RILEM TC 281-CCC interlaboratory test results showed [5] that beside the trowelled surface (top side), the bottom side also presented a significantly different carbonation depth compared to the other sides (trowelled surface or lateral sides) of mortar specimens, particularly when CEM II and CEM III were used as binders. However, a corresponding trend was not observed in concrete specimens. In the case of inducing accelerated carbonation in loaded concrete specimens, Yao et al. [36] reported that the carbonation of the bottom surface was only 1/3 of that of the top trowelled surface and the side surfaces. A similar effect has also been

observed in durability tests evaluating the sulfate resistance of mortars [37]. Therefore, it is preferable to measure the carbonation depth along the side surfaces, excluding the corners. The top and bottom surfaces should be excluded to minimise the effects of varying surface qualities and sample inhomogeneity resulting from the casting process.

For obtaining drilled samples from concrete structures, the standard EN 12504-1 [38] is the procedure that is typically followed, and is cited in the CEN carbonation standards (e.g. EN 12390-12). Detailed procedures for obtaining drilled samples are not provided in the other carbonation standards evaluated here, with the exception of SIA 262/1 [29] where
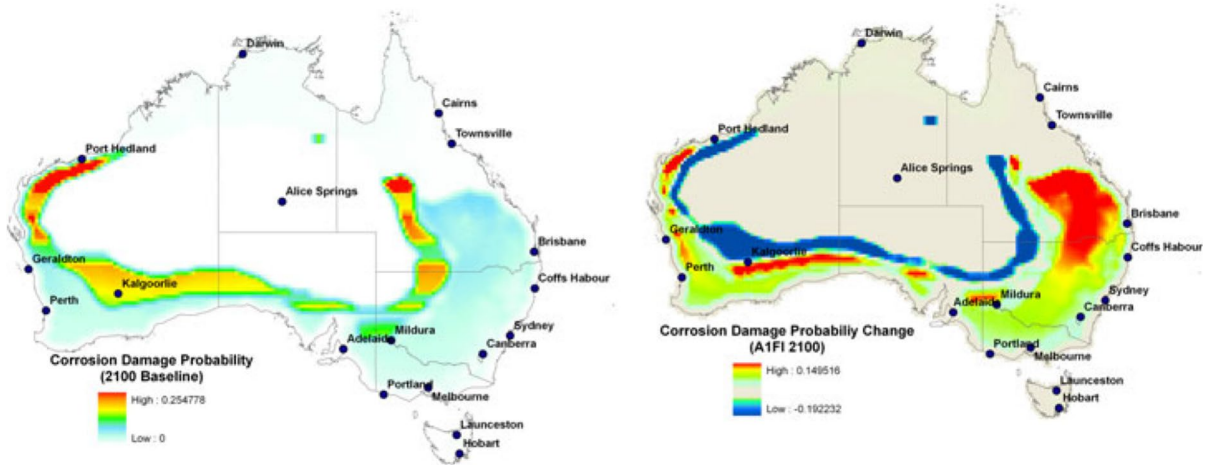
Fig. 3 Maps showing the probability of carbonation induced corrosion of concrete structures in Australia by 2100. **a** Probability of corrosion damage without consideration of climate change, and **b** change in probability of corrosion damage for IPCC A1FI emission scenario. Reproduced from [3], copyright Springer Science + Business Media B.V.

drilling of samples with a minimum size of 50 (diameter) × 100 (length) mm is described. ASTM C42 [39] also describes drilling of core samples, but with a specific focus on obtaining specimens for strength testing.

In addition to the various shapes of concrete specimens, the shortest dimension of the concrete/ mortar specimen specified in norms, and used in different studies, varies from 40 up to 120 mm depending on the maximum size of the used coarse aggregate as shown in Fig. 4.

Some standards do not provide specific dimensions of the concrete specimen, but instead indicate that the shortest dimension of the specimens must be at least three or four times the maximum nominal aggregate size [8, 17, 22]. However, such low ratios between specimen and maximum aggregate size are less conservative than common norms such as the ACI 318-19 [55] for producing concrete, where the maximum size of the coarse aggregate is limited to one-fifth of the narrowest dimension of the samples. Most published studies on carbonation used sample dimensions that met both the requirement of the carbonation standards, and the requirements of the norms for concrete production. While the ratio of sample dimension to maximum aggregate size is expected to have a minor influence on carbonation depth itself, a very low ratio will increase the variability of the results.

3.2 Specified curing age and conditions prior to pre-conditioning and testing

Prior to exposing specimens to CO_2, most of the standards recommend specific conditions and durations of curing and/or pre-conditioning. This is done with the aim of allowing the binder or matrix in the concrete to achieve a microstructural maturity that will be roughly representative of the material during service, and to ensure that the degree of internal saturation (relative humidity) of the material is homogenised, so carbonation can actually proceed (and is not affected by zones of different internal RH). The intention is that different samples can be compared with each other in an equitable manner—although this is not always possible when the materials being tested are of very different chemistry or microstructure. From a CO_2 transport perspective, it is well known that the relative humidity or degree of saturation of the concrete plays a key role in the carbonation progress. When the pore structure is saturated with water this prevents CO_2 from entering the material, and conversely, when the pore structure is completely dried, although the diffusivity of CO_2 increases, there is not sufficient pore water for CO_2 to dissolve to form carbonic acid and trigger the carbonation reaction [56]. This will be discussed in more detail in Sect. 3.3.

Table 2 Selected examples of sample geometry and dimensions specified in different carbonation standards

Test	Specimen specifications/curing	References
BSI 1881-210:2013	For a single determination of carbonation depth, 100 mm or greater cubes may be used. Ensure that the shortest dimension of the prism/cube is not less than 4 times the maximum nominal upper aggregate size	[31]
	Prisms not less than 280 mm long with a cross-section of not less than 70 mm × 70 mm may be used, from which slices approximately 50 mm thick can be split off at each date of carbonation testing	
EN 13295:2004	Prisms with minimum dimensions of 40 mm × 40 mm × 160 mm shall be used. For concrete with a maximum aggregate size > 10 mm, prisms with minimum dimensions of 100 mm × 100 mm × 400 mm shall be used. The test is carried out on two parallel specimens (and compared with two specimens of control concrete). For each measurement, a slice with a thickness > 15 mm is broken off the prisms	[19]
GB T50082-2009	Rectangular prism (length to width ratio > 3) samples are preferred, with three replicates included in each test group. Cubes can be used as alternatives. The number of replicates included in each test group then needs to be increased, given that each cube sample can only be tested once	[16]
ISO 1920-12:2015	For the determination of the depth of carbonation at one exposure period, two cubic specimens having a cross-section of 100 mm or greater shall be prepared. For the determination of the depth of carbonation at more than one exposure period on the same test specimen, two prisms, 400 mm long and having a cross-section of 100×100 mm^2 shall be prepared	[22]
	The shortest dimension of the specimen, cube or prism, shall not be less than four times the maximum nominal upper aggregate size	
IS 516 (Part-2/Sec 4) 2021	For the determination of the depth of carbonation at any given exposure period, two cube specimens having a cross-section of 100 mm or 150 mm shall be prepared	[24]
	For the determination of the depth of carbonation at more than one exposure period on the same test specimen, two prisms, 500 mm long and having a cross-section of 100×100 mm^2, shall be prepared	
NT Build 357:1989[a]	The test may be carried out on laboratory cast concrete or mortar specimens of various shapes. Specimen may, in the case of concrete, be either of the cylinder type with diameter 100 mm and length 200–300 mm, or prisms with cross section 100×100 mm^2 and length 300–500 mm	[25]
	In the case of mortar, the RILEM prism type of $40 \times 40 \times 160$ mm^3 size may be used. The test is carried out in parallel on 2 or 3 samples	
RILEM CPC-18:1988	Concrete prisms with a cross-section of 100×100 mm^2 that can be split into lengths of roughly 50 mm, for each date of testing, are suitable. For mortar, prisms $40 \times 40 \times 160$ mm^3 are recommended from which a slice of roughly 20 mm is split off at each date of testing. In no case shall the shortest dimension of the prism be less than 3 times maximum aggregate size	[8]
SIA 262/1: 2019	For prisms, the test is carried out with 1 prism measuring $120 \times 120 \times 360$ mm^3	[29]
	For cores, 4 cores (1 drill core per test date) with a diameter of ≥ 50 mm and a length of ≥ 100 mm are required	
UNE83993-2:2013	The specimens to be tested can be cylinders or prisms. In both cases the ends of the samples need to be flat and perpendicular to its central axis. They must have a diameter (in the case of cylindrical samples) or side (in the case of prisms) of at least 75 mm and a length ≥ 150 mm	[28]
UNI 9944:1992	Concrete specimens are drilled from pre-existing structures in the form of cylinders (dimensions are not specified)	[23]

[a]Similar specimen sizes are recommended by the LNCE 391

Curing and pre-conditioning of concrete specimens will affect the degree of Portland cement hydration and latent hydraulic and pozzolanic reactions, and thus the amount of hydrates formed and the resulting pore structure. This will be more significant in concrete with some SCMs, as it is well-known that they
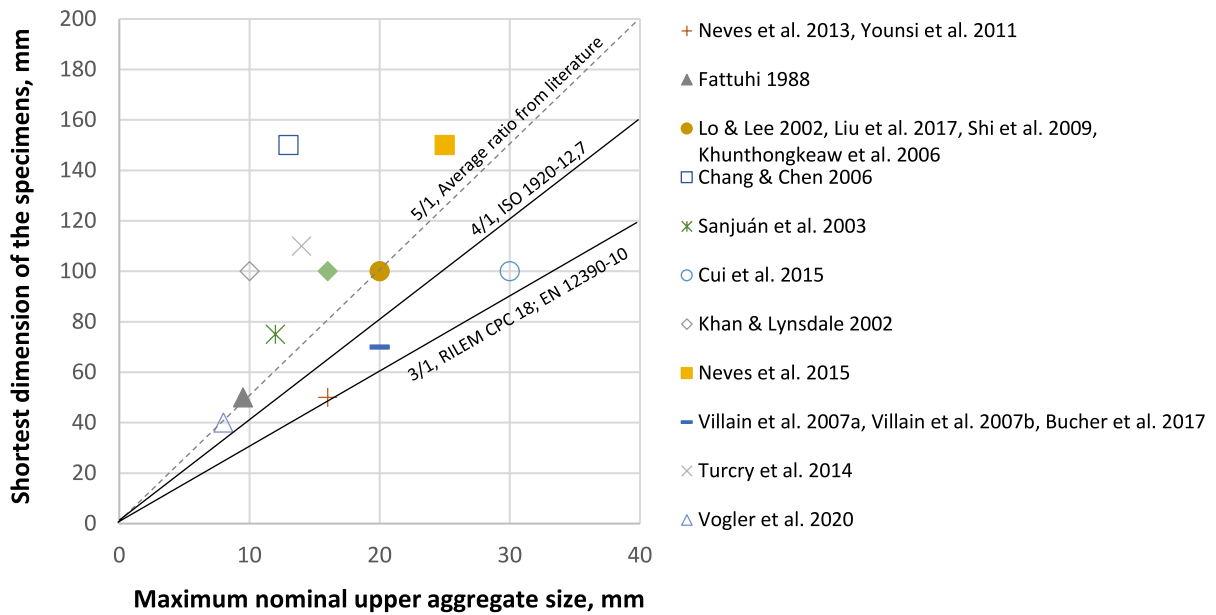
Fig. 4 Sample dimensions used for carbonation experiments on concrete samples. The lines indicate the relationship of the smallest dimension of the specimen to the maximum aggregate size specified in standards ISO 1920-12, EN 12390-10:2018 and RILEM CPC-18. Data obtained from Neves et al. [40], Younsi et al. [41]; Fattuhi [42]; Lo et al. [43]; Liu et al. [44]; Shi et al. [45]; Khunthingkaw et al. [46]; Chang et al. [47]; Sanjuán et al. [15]; Cui et al. [48]; Khan et al. [49]; Neves et al. [50]; Villain et al. [51, 52]; Bucher et al. [53]; Turcry et al. [13]; Vogler et al. [54]

generally show later strength development compared with plain Portland cement concrete [57, 58]. Any differences in curing or pre-conditioning methods and durations will impact the measured carbonation resistance of the material. Although very different types of curing methods or sample pre-conditioning are specified in various carbonation standards (Table 3) or in published studies, including water curing, moist curing, air curing, sealed curing, saturated lime bath curing, heat curing and even using curing compounds, very little research on the influence of curing types on carbonation resistance is available in the literature, as reviewed in [59, 60].

Ekolu et al. [61] concluded that the use of different common curing methods (with similar duration) led to similar carbonation behaviour in real structures. A similar conclusion was reached by RILEM TC 281-CCC as part of the round robin test evaluating carbonation performance of concrete under different standardised test methods [5]. Similar concrete rankings (i.e. placing the samples with different cement types in order from more to less resistant to carbonation) were achieved when adopting different curing methods. However, predefined sealed curing for 28 days at 20 °C resulted in higher carbonation depths compared to those measured in specimens cured for 28 days under water, especially for CEM I samples (e.g. the results indicate 60% higher carbonation depths for CEM I concrete samples vs. 19% higher for CEM III concrete). On the other hand, samples water-cured for 3 or 7 days rather than 28 days exhibited larger carbonation than those sealed cured, with the magnitude of the difference depending on the cement type [5]. This highlights that investigation of the potential effects of curing and pre-conditioning is required for adoption of more complex concrete mix designs with increased use of SCMs.

The curing duration is a well-known parameter that has a significant impact on carbonation resistance, particularly for blended cements with SCMs, and this is closely linked to the matrix maturity achieved as the material ages. A detailed review of 287 papers on carbonation of concretes containing blast furnace slag [62] identified significant variations in the curing duration prior to testing. 50% of the papers used a curing duration between 1–14 days, 29% between 15–28 days, 6% between 56–91 days, 3% more than 91 days, and for the remaining 12% no

Table 3 Selected examples of sample curing and pre-conditioning recommendations included in existing carbonation testing standards. If indicated in the standards, a clear distinction between natural or accelerated carbonation testing is included in the table

Test	Specimens preconditioning required	References
BSI 1881-210:2013	Two concrete cubes are conditioned in a laboratory air environment for 14 days prior to sealing the top, bottom and two opposite side faces. After sealing of all but two faces, the cubes are placed in a storage chamber for a period of at least 70 days. When testing at more than one age, the prisms are conditioned in a laboratory air environment for 14 days prior to sealing the top, bottom and two end faces. After sealing all but two longitudinal faces, the prisms are placed in a storage chamber for the overall test period of at least 70 days	[31]
EN 13295:2004	Samples are cured in the moulds, covered with a plastic sheet, for 24 h. Subsequently, they are cured for further 27 days under water at (21 ± 2) °C. The sides of the specimens shall be free from contaminants (e.g. demoulding agents) which could influence the carbonation rate. Preconditioning is done by storing the specimens at (21 ± 2) °C/ (60 ± 10)% RH until the weight change within 24 h is less than 0.2%, at least for 14 days	[19]
CUR-Aanbeveling 48:2010	*Natural carbonation:* In three-day-old samples paraffin wax should be applied in three layers on the two end faces, the finish side and the opposite side. Immediately after the application of the paraffin wax, the specimens need to be exposed to laboratory atmosphere at a temperature of (20 ± 2) °C and a relative air humidity of 65 ± 5% up to the moment of testing *Accelerated carbonation:* At 28 days of age the samples are removed from the water bath and immediately stored for 14 days at (20 ± 2) °C and relative humidity of (65 ± 5)%. Afterwards paraffin wax should be applied in three layers in each specimen, on the two end faces (finishing side and the opposite side)	[30]
EN 12390-12:2020	At an age of 28 days, the prisms/cubes shall be removed from the water bath and transferred to a laboratory air drying environment (18 °C to 25 °C, 50–65% relative humidity) for 14 days. After 14 days of exposure to laboratory air, the test specimens shall be placed in the carbonation storage chamber. The prisms/cubes shall be positioned in a way that permits air to circulate freely around the faces where carbonation measurements are to be taken	[18]
GB T50082-2009	Samples after 28 days of curing under standard conditions should be used. For samples blended with supplementary cementitious materials (e.g. fly ash), extended curing time may apply. Samples need to be preconditioned at 60 °C for 48 h prior carbonation exposure. After preconditioning, the prisms will be coated in melted paraffin wax, only leaving one (or two opposite) side to be exposed to carbonation. On the exposure surface, draw paralleled lines along the longitudinal axis every 10 mm, to provide indication points for measuring carbonation depth. The distance between samples in the carbonation chamber should be more than 50 mm	[16]
ISO 1920-15	At an age of 28 days, the prisms/cubes shall be removed from the water bath and transferred for 14 days to a laboratory air drying environment having a temperature of (18–29) °C and relative humidity of (50–70) %. After 14 days conditioning, the top and bottom longitudinal faces and the two end faces of prisms (or top, bottom and two side faces of cubes) shall be sealed using paraffin wax or a similar material that will prevent ingress of carbon dioxide and allow carbonation on two cast longitudinal surfaces. Once the prisms/cubes have been sealed, they shall be placed in the storage chamber. The prisms/cubes shall be positioned in such a way that their exposed faces are vertical, and that permits air to circulate freely around the two faces that are to be carbonated	[22]
IS 516 (Part-2/Sec 4) 2021	The specimens shall be stored in water or in a chamber having a temperature in the range of 27 ± 2 °C and a minimum relative humidity (RH) of 95%. At an age of 28 days, the prisms/cubes shall be removed from the water bath and transferred for 14 days to a laboratory air drying environment having a temperature in the range of 27 ± 2 °C and RH in the range of 65 ± 5%	[24]

Table 3 (continued)

Test	Specimens preconditioning required	References
SIA 262/1: 2019	*Prisms:* The prism should be stored after stripping (usually after 1 day) until the age of (72 ± 6) h in water at a temperature between 15 °C and 25 °C. Thereafter, the prism must be stored in the climatic chamber up to the age of 28 days until the beginning of the test. If intermediate storage is necessary (for example, when casting the prism on the construction site), the prism should be protected from drying out (covered with a film, under water) until the age of (72 ± 6) h. If the prism is not immediately transported to the testing laboratory, it must be stored in a protected, dry environment (relative humidity $\leq 70\%$, temperature between 10 °C and 30 °C) until transported to the testing laboratory. However, it must be stored in the climatic chamber at the latest from the 10th day until the beginning of the test at the age of 28 days	[29]
	Cores: For the test, the exposed outside (A) and inside (I) (unweathered side or back) of the cores are used. The inside of the cores must be flat and perpendicular to the specimen axis. If necessary, it must be cut. Drill cores are placed in the climate chamber for 3 weeks prior to the test. The lateral surfaces of the cores are covered or coated with a CO_2-dense material before the start of the test	
UNE83993-2: 1993	Once the specimens have reached the desired testing age, they need to be pre-conditioned. This consists in drying the specimens at 40 °C for a week, following this by sealing and storing the specimens at 20 °C for three weeks. This means that the sample preconditioning lasts 28 days in addition to the curing time. Once the samples are conditioned, they are placed in an environmental chamber, ensuring that at least 90% of the sample surface is exposed to the air (this can be achieved by using a rigid plastic mesh, for example). The specimens must be at least 10 cm separated from each other	[28]

curing duration was mentioned. Only a few studies have compared the effect of different curing durations on carbonation resistance of the comparable concrete [42, 43, 63–65]. An example of the significant influence of curing duration on carbonation is shown in Fig. 5 [64], where it can be seen that in the case of slag-containing concretes, at contents of 50 wt.% slag, significant changes in carbonation depth are observed with differences in curing duration from 1 to 18 months.

Generally, the minimum duration of curing required for realistic evaluation of the carbonation performance of a concrete is dependent on the cement replacement level, the type of SCM used, and the exposure CO_2 concentration. Currently, insufficient systematic investigations are available to define the minimum acceptable curing duration for concrete containing SCMs and/or cured under different exposure conditions. The ingress of CO_2 depends on the degree of hydration and the consequent pore structure formed at the time of exposure. Considering that blended Portland cement concretes have a different microstructure and phase assemblage, and are generally less mature compared to Portland cement concrete at a specified early curing time (e.g. 28 days), they are almost inevitably more prone to carbonation

when tested at such ages. Since construction practice recommends longer curing for concrete with SCMs [66], durability testing standards need to be modified accordingly. It must also be considered that under natural carbonation conditions, the carbonation takes place over a longer time span, when the SCM-containing concrete is already more mature. For long term prediction of natural carbonation from accelerated carbonation results, *fib* Bulletin 34 [67] recommends accounting for curing duration using a curing factor (Kc), which is not well quantified or reported for new SCMs.

3.3 Influence of pre-conditioning period

At the end of a recommended curing period, additional pre-conditioning prior to carbonation exposure is required by some standards (for example XP P18 458 [21], BSI 1881-210 [31], CUR-Aanbeveling 48 [30], EN 12390-10 [17], EN 12390-12 [18] and others). This step generally includes storage of the samples at natural CO_2 concentrations at similar temperature and relative humidity (RH) to that of the accelerated carbonation testing period (Table 3). The aim of such pre-treatment is to homogenise the internal water saturation of concrete to facilitate the
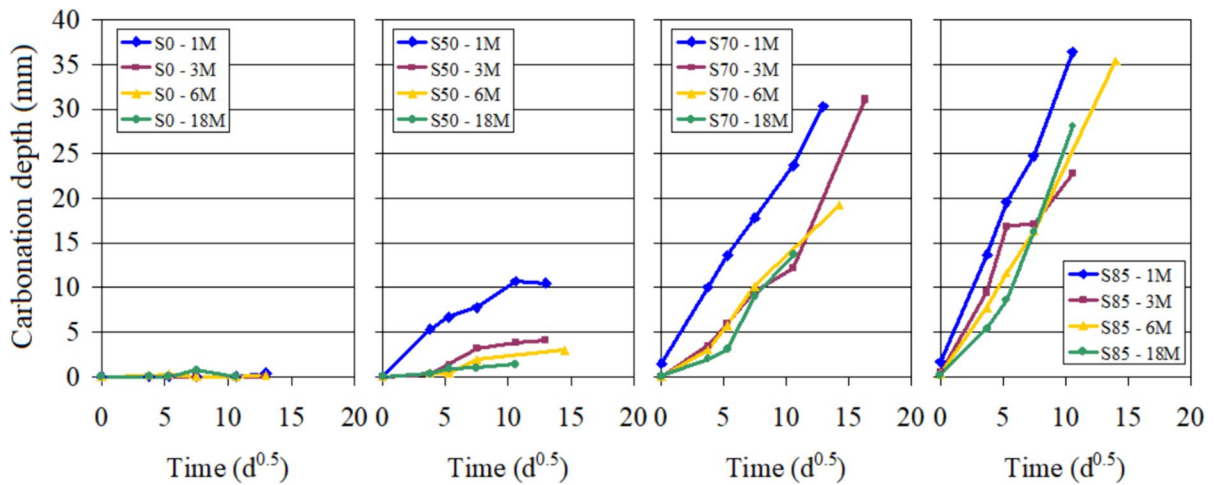
Fig. 5 Effect of curing duration (1, 3, 6 or 18 months at ~20 °C and > 95% RH) on the carbonation depth of concrete with 0, 50, 70 and 85 wt.% replacement of Portland cements by BFS (denoted as S in the legend), exposed to 10 vol.% CO_2. Reproduced with permission from [64], copyright Elsevier B.V.

ingress of CO_2 into the material. This might only partially be guaranteed as concrete density and pore structure will impact transport properties. For example, Shi [68] reported that drying of 20 mm thick specimens containing 31.9 wt.% metakaolin at 50 °C to constant weight took roughly 65 days, much longer than drying of Portland cement specimens which took only 10 days. For natural carbonation conditions, preconditioning is generally not considered to be necessary, since (i) carbonation kinetics are slower than the evaporation of water from wet concrete; (ii) preconditioning under a CO_2-free environment is not always feasible for concrete samples; and (iii) real concrete infrastructure elements are usually not preconditioned, except possibly for some precast concrete elements.

Pre-conditioning is crucial for accelerated carbonation testing, to avoid any differences in the performance due to exposure of concrete at levels of internal RH dissimilar to those applied during the accelerated carbonation testing. The influence of pre-conditioning before carbonation in accelerated carbonation experiments has been less explored than the effect of curing duration, and its necessity remains debatable. Lye et al. [62] evaluated 198 papers on carbonation of slag concretes, identifying that only 1/3 of the papers mentioned that preconditioning of the concrete samples was applied. This highlights that differences in carbonation rates reported in different studies cannot always be explained simply on the basis of the chemistry of the binder or concrete strength class, as these can also be influenced by differences in sample curing and pre-conditioning. In particular, the internal relative humidity influences the microstructure development at a young age as well as the carbonation kinetics. The water saturation degree of concrete will also play a key role in the diffusivity of CO_2, which will also be influenced by the pre-conditioning step. Artificially creating a homogeneous moisture distribution might not be representative of the actual performances of materials; however, accelerated tests aim to simulate a worst-case scenario. There is still need for research to understand and quantify the effect of pre-conditioning and RH on (accelerated) carbonation for evolving SCMs.

RILEM TC 116-PCD developed a recommendation for moisture redistribution pre-conditioning [69] for the measurement of the gas permeability and capillary absorption. This procedure consists of pre-drying of the concrete test specimens to an intermediate/average moisture concentration, which is in equilibrium and results in a uniform distribution of the evaporable water in the test specimens. This is achieved by storing the specimens at 50 °C either sealed or in 'small sample containers', for a minimum of 14 days. A revision of this recommendation was made, and an improved procedure was then proposed which also included a redistribution/homogenisation step at

50 °C [70]. This proposed approach could be considered for sample pre-conditioning prior to carbonation testing, as this methodology has been proven to be more effective to ensure homogeneous moisture distributions in cementitious materials.

4 Specified accelerated carbonation exposure conditions

The accelerated carbonation exposure conditions are the main variables across different studies evaluating carbonation performance of concrete, and therefore their effect on the results obtained from such tests needs to be critically evaluated. As mentioned earlier, a round robin test conducted by RILEM TC 281-CCC [5], assessing carbonation performance of concrete produced with Portland, Portland-fly ash and blast-furnace slag blended cements, and adopting different standardised testing protocols, demonstrated how different exposure conditions enabled similar rankings of the concrete evaluated but led to significant differences in the carbonation rates recorded. In the following sections the variability of exposure conditions recommended by different standards and their effect on the results obtained will be briefly described.

4.1 CO_2 concentration

As indicated in Table 4, the exposure conditions used during carbonation testing vary significantly from test to test, particularly the CO_2 concentrations adopted. CO_2 concentrations in accelerated tests range from 1 to 20%, but most of the standards prescribe CO_2 levels between 1 and 5%. There were only two standards recommending testing above such CO_2 concentrations: (i) the previous French standard recommended 50% CO_2 (XP P18 458:2008), which changed in 2022 to 3% (XP P18 458:2022-12) in agreement with the European standard, and (ii) the Chinese standard (GB T50082-2009), which recommends testing at 20% CO_2.

It is anticipated that at a higher CO_2 exposure concentration, the carbonation front will progress faster (Fig. 6) and assessment of the carbonation performance can take place in a shorter timeframe. However, the mechanism of carbonation and consequently the phase assemblage of the hydrated cement matrix can change significantly at a higher CO_2 exposure concentration, which will not represent the carbonation mechanism occurring in a natural environment. The effects of different exposure conditions on phase assemblage have been discussed in detail in the literature review by von Greve-Dierfeld et al. [2] and will only be briefly mentioned here.

There is no consensus neither in standards nor in the literature regarding maximum CO_2 concentrations to be applied in accelerated tests so that similar carbonation reaction products to those identified in pastes exposed to natural carbonation are forming. For example, Liu et al. [71] identified in carbonated Portland cement specimens that the preferential

Table 4 Selected examples of exposure conditions recommended by accelerated carbonation standards

| Standard ID	Exposure conditions			
	CO_2 concentration (%)	Temperature (°C)	Relative humidity (%)	References
XP P18 458:2022	3.0 ± 0.5	20 ± 2	65 ± 5	[21]
BSI 1881-210:2013	4.0 ± 0.5	20 ± 2	55 ± 5	[31]
CUR-Aanbeveling 48:2010	4.0 ± 0.5	20 ± 2	55 ± 5	[30]
EN 12390-12:2020	3.0 ± 0.50	20 ± 2	57 ± 3	[18]
EN 13295:2004	1.0	21 ± 2	60 ± 10	[19]
GB T50082-2009	20	20 ± 2	70 ± 5	[16]
ISO 1920-12	4.0 ± 0.5	20 ± 2	55 ± 5	[22]
IS 516 (Part-2/Sec 4) 2021	3.0 ± 0.5	27 ± 2	65 ± 5	[24]
LNEC E391:1993	5.0 ± 0.1	23 ± 3	55–65	[26]
SIA 262/1:2019	4.0 ± 0.1	20 ± 2	57 ± 3	[29]
UNE 83993-2:2013	3.0 ± 0.4	20 ± 2	65 ± 5	[28]
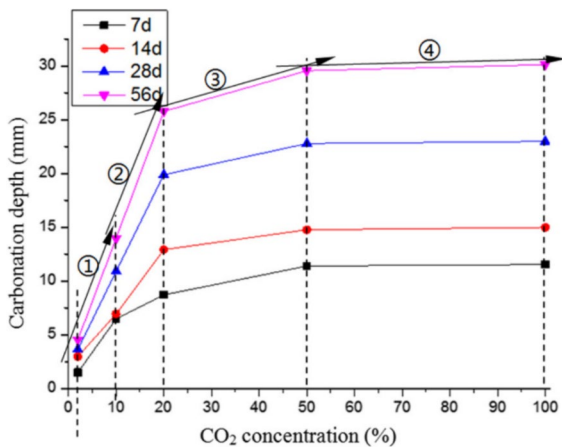
Fig. 6 Effect of CO_2 concentration on carbonation depth of a Portland cement concrete with a 28d compressive strength of 30 MPa, as a function of curing time. Reproduced with permission from [48], copyright Elsevier B.V.

calcium carbonate polymorph forming was strongly dependent on the degree of calcium silicate hydrate (C–S–H) carbonation and the carbonation duration, which were not strongly affected by the CO_2 concentration (being 0.03%, 3%, 10%, 20% 50% and 100% in their research), although C–S–H decalcification is more pronounced in accelerated conditions. However, it should be noted that besides temperature and CO_2 concentration, the internal RH as well as the composition of the pore solution significantly influence changes in phase assemblage and microstructure during carbonation. Based on the finding that the ratio of decalcified to remaining C–S–H was similar for tests at 3% and 20% CO_2, it was then concluded that a CO_2 level up to 20% can be applied in accelerated tests. Figure 6 shows the effect of the CO_2 concentration on carbonation depth of Portland cement concrete, measured at different curing and exposure times, as obtained by Cui et al. [48]. It was identified that the carbonation depth increases linearly at CO_2 exposure concentrations up to 20%, and does not change significantly beyond 20%, which was attributed to the dense surface layer formed upon carbonation, lowering the CO_2 diffusion. These observations have been used to limit the CO_2 concentration up to 20% for prediction of natural carbonation based on accelerated tests. This CO_2 concentration is the one recommended by the Chinese standard (GB T50082-2009, [16]).

Castellotte et al. [72] conducted a study using 0.03%, 3%, 10% and 100% CO_2 concentrations on pastes with Portland cement with low alumina content, and 5% addition of limestone. They showed that up to 3% CO_2 exposure no significant changes occurred in the type of reaction products formed upon carbonation, with comparable Ca/Si ratios to those identified in naturally carbonated conditions, while ettringite and anhydrous cement remained present in both cases. For CO_2 levels of 10% or higher, significant changes were detected. Comparable results were also identified by Auroy et al. [73] when evaluating Portland cement pastes, concluding that using 3% CO_2 made it possible to reach a carbonation state that was representative of long-term carbonation in natural conditions. Another aspect that should be taken into account when selecting a suitable CO_2 level in accelerated tests is the release of water upon carbonation [74, 75] which can block the capillary pores and hinder CO_2 diffusion. This effect was investigated by Van den Heede et al. [76] in fly ash blended concrete, who identified that carbonation-induced water formation at different CO_2 exposure concentrations (0.04%, 1% or 10% CO_2) affects carbonation progress, and using a concentration of 10% CO_2 was considered too high to simulate natural carbonation. Carbonation shrinkage is also likely to increase at higher CO_2 exposure concentrations [77].

Results from the RILEM TC 281-CCC round robin test on the effect of carbonation depths as a function of the CO_2 carbonation exposure conditions are shown in Fig. 7 for CEM II- and CEM III-containing concretes. It can be clearly seen that independent of the type of concrete evaluated, the differences in CO_2 concentration during carbonation testing will lead to different carbonation depth values. From this study it was not possible to draw a clear conclusion regarding the effect of the CO_2 concentration in isolation, as each of the different standardised testing methods adopted also presented variabilities regarding sample pre-conditioning period and conditions. Nevertheless, there seems to be a clearer trend in the results of the CEM III concrete where a reduced carbonation depth variability is observed, and higher CO_2 concentrations lead to higher carbonation depths.

Several standards recommend an exposure concentration of 4% CO_2 or above. However, awareness of the impact of CO_2 concentration in carbonation testing is increasing. The European standard for
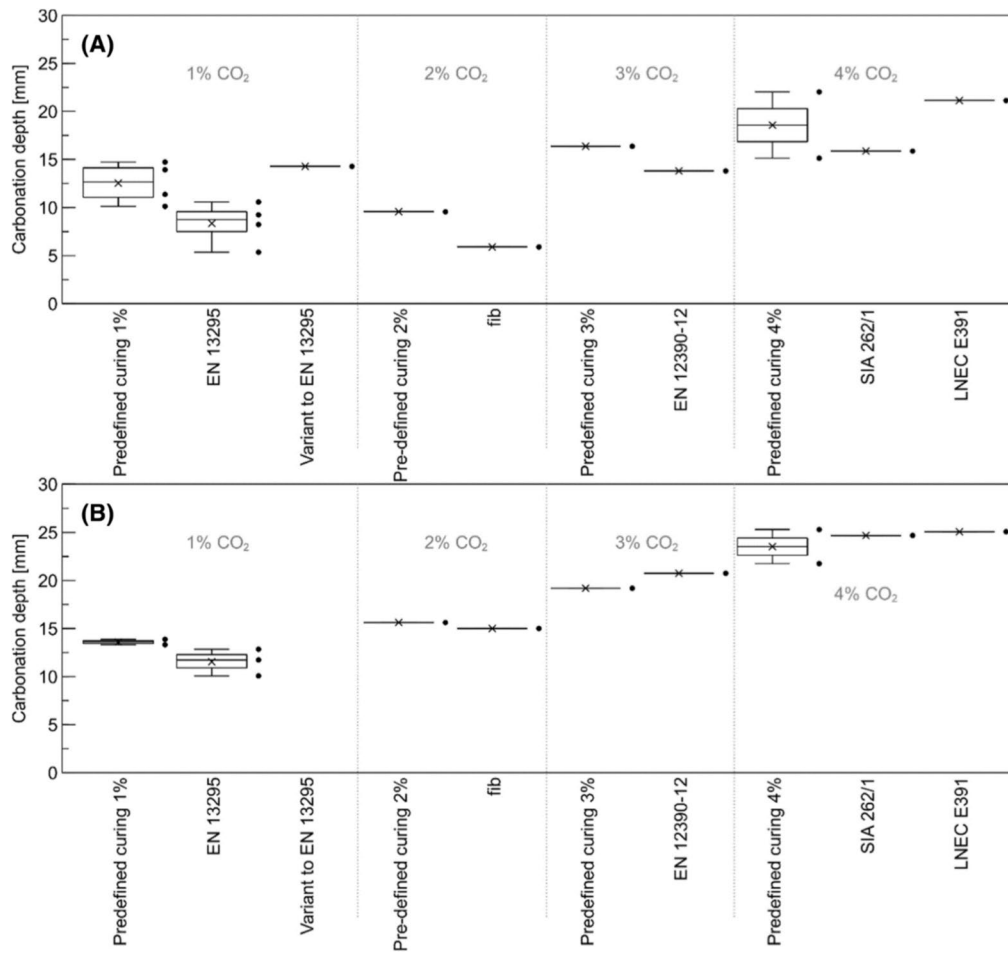
Fig. 7 Box-and-whisker plot and the individual mean per laboratory of the carbonation depths of concrete measured after 91 days of accelerated carbonation for **A** CEM II and **B** CEM III, grouped by the applied accelerated carbonation method.

Reproduced from [5], copyright RILEM. It is noted that the LNCE E391 recommend exposing specimens at 5% CO_2 (Table 4) rather than 4% CO_2

accelerated carbonation testing (EN 12390-12) had a reduction in the CO_2 concentration from 4 to 3% in its recent revision in 2020, and the French standard (XP P18-458) reduced the CO_2 concentration of exposure from 50 to 3% in 2022. Further studies need to be conducted to understand the influence of this parameter specifically for concretes containing SCMs, and the suitability of existing accelerated carbonation testing methods in determining their carbonation potential under service conditions.

4.2 Relative humidity (RH) and temperature

Table 4 shows that the specified RH during accelerated carbonation testing can vary from 55 to 70%. It is generally accepted for Portland cement based materials that carbonation will take place at humidity ranges between 50% as a lower limit, and 70 [78] or 80% [79] as an upper limit. A low humidity does not allow sufficient dissolution of CO_2 to form carbonic acid, and high humidity hinders the diffusion of CO_2. The RH ranges adopted in standards are broad, which means that adopting either the lower or upper limiting values of a particular standard can have significant effects on the carbonation results [79]. A detailed

discussion of the effect of RH and temperature on the phase assemblages of cementitious materials with SCMs under carbonation is reported in [2]. One of the main outcomes of this analysis is that for materials containing SCMs, the RH range at which carbonation proceeds the fastest may differ from the values determined for Portland cement.

It is also worth noting that the RH of the exposure environment does not necessarily correspond to the internal relative humidity in the concrete. Upon drying, a gradient in the internal humidity exists between the inner and the outer layers. This is dependent on the moisture transport, which in turn is influenced by the microstructure of the concrete [80]. Also, the effect of temperature and carbonation-induced water formation will influence internal gradients in the moisture distribution. Pre-conditioning of specimens before accelerated carbonation tests (as discussed in Sect. 3.3) is typically conducted to minimise such effects. The fact that measuring internal RH gradients in specimens prior or during carbonation is not a conventional practice means that there is uncertainty about the effectiveness of the pre-conditioning or RH exposure conditions in ensuring that a certain degree of saturation of the specimens is achieved upon testing [70].

There is more consistency in the recommended testing temperature across the different standardised testing methods (Table 4). The majority of carbonation standards specify a temperature of ~20 °C. Although this temperature is far from being representative of all micro-climates in which carbonation can occur, this is a conventional value adopted for the testing of construction materials in controlled laboratory conditions. For example, IS 516-2 recommends 27 ± 2 °C, which is the standard laboratory temperature in Indian standards, and also relevant to the temperature conditions in other hot or tropical countries (see Table 4). It is important to consider that the temperature during CO_2 exposure will have an impact on the carbonation rate [2]. Figure 8 illustrates how carbonation depth can change as a function of the temperature of exposure, for concretes of different strength classes.

Currently, only the ISO standard [22] and IS 516 [24] provide a specification for adopting 27 °C for simulating tropical climate conditions. The significant differences between the exposure temperatures under natural environmental conditions and accelerated

carbonation standardised tests will create significant deviations in the carbonation kinetics and results derived from those tests [81]. This has implications for predicting natural carbonation potential from accelerated carbonation results, which is often overlooked but will be discussed in more detail in Sect. 6.

5 Determining changes in alkalinity (pH indicators)

All the existing testing standards evaluating carbonation performance of concrete recommend the use of a pH indicator, mostly phenolphthalein, to determine the changes in pH associated with the carbonation reaction, particularly the carbonation of portlandite. Such measurements are accepted as representative of the carbonation depth. The phenolphthalein indicator shows colour changes at pH between 8.2–10.0 in solution. The main difference across standardised testing methods is in the preparation of the phenolphthalein solution as well as how and when the readings need to be performed. Most standards (e.g. BSI 1881-210, CUR-Aanbeveling 48, EN 12390-10, EN 12390-12, EN 13295, ISO 1920-12, SIA 262/1, UNE83993-1, RILEM CPC-18, LNEC E391) specify dissolving 1 g of phenolphthalein powder in
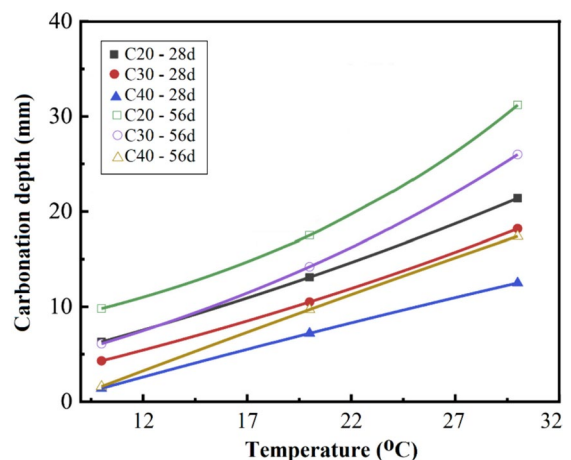

Fig. 8 Curves of carbonation depth of fly ash blended concretes of different strength classes (indicated as 'C' in the legend) exposed to 20% CO_2 and 70% relative humidity for 28d or 56d of exposure, versus temperature. The days in the legend represent the carbonation exposure time. Adapted from [44]

Fig. 9 Photographs of partially carbonated **A** Portland cement concrete, and **B** concrete containing calcined clays, after spraying with a 0.1% phenolphthalein solution produced with **A** 70% isopropanol + 30% distilled water and **B** 100% isopropanol. The photographs were taken immediately after spraying the concrete with the indicator solution. Courtesy of Y. Dhandapani
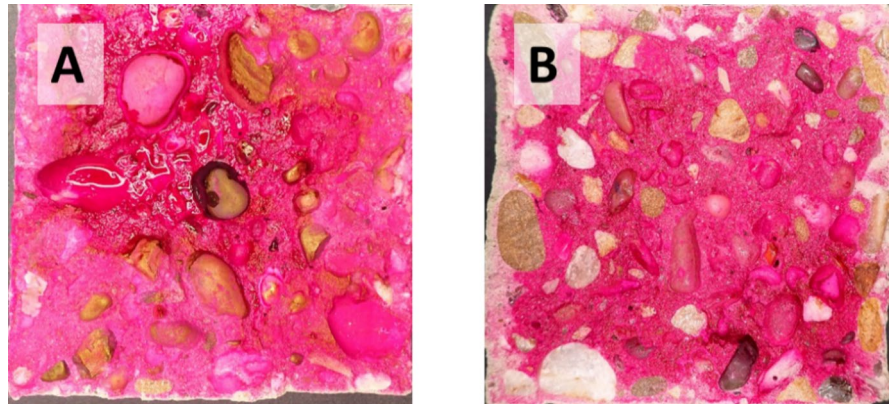
100 mL of a mixed solvent (70 mL isopropanol or ethanol + 30 mL distilled or deionised water). The Spanish standards (UNI 9944) recommend 0.1% of phenolphthalein in isopropanol, while the Chinese standard (GB T50082) specifies a 1% phenolphthalein solution prepared in water diluted ethanol (ethanol to water ratio 4:1). The Norwegian test (NT Build 357) recommends dissolving 1 g phenolphthalein in 500 mL of distilled/ion exchanged water and 500 mL ethanol.

In concrete with SCMs it has been identified that there are issues with clearly identifying colour change boundaries, and therefore the carbonation depth, when using phenolphthalein solutions produced as per recommended standards (mixed solvents), e.g. Figure 9A. This has been attributed to the potential leaching of alkalis (Na^+/K^+) in the carbonated region [5]. This is not the case when using an isopropanol or ethanol solution without addition of water, where well defined areas of discoloration are detected (Fig. 9B). The application of indicators to concrete produced from blast furnace slag-containing cements may also be problematic due to the very dark colour of the hydrate regions in some slag cement concretes [82], as the indicator colour changes are difficult to see against the background of a dark green material, and the carbonation front may or may not correspond with other colour changes that take place in the specimens due to redox processes in the cement itself.

An overview of the recommendations included in different standards for collecting the carbonation measurements is reported in Table 5. The times when the readings need to be performed, in terms of carbonation duration or for revealing the pH changes, vary depending on the standard (or in some cases are

not clearly specified), which will introduce significant variability between different studies and measurements. A clear example of such variability was identified during the RILEM TC 281-CCC round robin testing programme [5], where it was observed that, when using a phenolphthalein solution in 70% isopropanol/30% water, the time when the carbonation depths are measured (24 h, as in the RILEM CPC-18 method, instead of 1 h as recommended in EN 12390-12, see Table 5) was crucial for clearly distinguishing pH changes, particularly in CEM I and CEM II mortars or concretes. Perhaps of all the variables discussed here, the timing of when the carbonation depth needs to be measured is the most relevant, because if no clear boundary is observed, the measurements will not be reliable. Further investigation into the impact of when and how carbonation measurements are collected is required, so standards can be modified accordingly.

Thiel et al. [83] evaluated the effectiveness of using other pH indicators (0.5% curcumin, 0.1% thymolphthalein, rainbow indicator) and identified that the colour of the thymolphthalein indicator faded after 24 h, and consequently recommended shorter times after spraying for collecting carbonation depth data. They also estimated that phenolphthalein underestimated carbonation (associated with consumption of portlandite) by about 20%, compared with the carbonation depths determined by analytical techniques such as thermogravimetry or laser ablation inductively coupled plasma mass spectroscopy. It is well-known that all calcium-bearing hydrated and anhydrous phases present in the concrete matrix will eventually carbonate [2], but the extent of carbonation

Table 5 Examples of carbonation measurement guidelines, and precision requirements of such measurements described in standard-ised testing methods

Test	Carbonation reading
BSI 1881-210:2013	After 70 days exposure, the cubes are split in half perpendicular to the exposed faces, and the depth of carbonation is measured in accordance with RILEM CPC-18, giving a single determination of the depth of accelerated carbonation. After each exposure period, a 50 mm slice is broken from each prism and tested for carbonation depth. After splitting off a slice, the split end faces of the prisms are sealed and the remainder of the prisms returned to the storage chamber
CUR-Aanbeveling 48:2010	*Natural carbonation*: The carbonation depth must be determined on each specimen at a 91-day of exposure on the fresh fracture surface of a split slab according to RILEM CPC-18. Additional measurements at 182 and 364 days of exposure are recommended for concrete with blast furnace slag or pulverized coal fly ash
	Accelerated carbonation: After 56 days of exposure the carbonation depth of the specimens must be determined on the fresh fracture surface of a split slab according to RILEM CPC-18. On each side, the carbonation depth must be determined at five positions evenly distributed along the length of the side. The depth should be measured with an accuracy of 0.5 mm per position. The result for each specimen is the average of the ten measurement values. The end face of the specimens must be re-coated with three layers of paraffin wax after the slab has been split
EN 12390-10:2018	After defined periods of exposure, an approximately 50 mm thick slice of the beam is broken off at each test age and tested for its carbonation depth. If cubes are being used, they are broken in half and one half of each cube is used to measure the carbonation depth, the other half being discarded. The carbonation depth is measured at three locations on each face of each beam/cube giving a potential total of 12 measurements per specimen and potentially 24 measurements for the two specimens. The mean carbonation depth of all measurements is calculated. The remains of the beams are returned to the climate-controlled chamber for testing at other pre-defined ages. Using at least three sets of measurements taken at 3 months, 6 months and 1 year, the rate of carbonation expressed as mm/$\sqrt{\text{year}}$ is determined. If the measured depth of carbonation is less than 5 mm at one year, the testing should be extended to two years
EN 12390-12:2020	The carbonation depth of slices from the prisms or two of the cubes shall be measured after 7, 28 and 70 days of exposure. A slice approximately 50 mm thick shall be broken off the prism after each exposure period and the rest of the prism returned to the storage chamber. The cubes shall be split in half parallel to the trowelled face. The depths of carbonation on the freshly broken surface of the split slice of the prism or one half of the cube shall be measured. Clear the broken surface immediately of dust and loose particles after breaking, and then spray with a fine mist of indicator solution. Avoid the formation of flow channels on the test surface. If only a weak colouration or none at all appears on the treated surface, spray again after 30 min. The measurements shall begin at 1 h $\pm$ 15 min after first spraying and completed without a pause, or if the readings cannot be started within this period, use a fixing solution to retain the colour without change. Where a fixing solution has been used, the timing of the depth measurements is not critical
EN 13295:2004	Carbonation depth shall be measured at the end of the drying conditioning and then after 56 days in the cabinet. Carbonation shall be measured on freshly broken faces from each prism
	For each measurement, a slice of 15 mm minimum thickness shall be broken off the prism using the chisel and the piece sprayed with the phenolphthalein indicator solution. Measurements of the depth of carbonation shall then be made 60 $\pm$ 5 min after spraying. The carbonation depth for the specimen is the average depth on all four sides
EN 14630:2016	Cores shall be split along their longitudinal axis and as nearly as possible across the diameter of the core. Large fragments (normally those with a smallest dimension of approximately 50 mm) shall be split as nearly as possible perpendicularly to the original external concrete surface; smaller fragments should not be split further but tested immediately after they are removed from the structure
	The freshly broken surfaces shall be cleared of any dust and loose particles without the use of water or abrasion and shall be sprayed with just enough phenolphthalein indicator solution to wet the surface without running down the surface. The test shall be completed as soon as possible after splitting the concrete face

Table 5 (continued)

Test	Carbonation reading
GB T50082-2009	Carbonation depths are measured after 3d, 7d and 28 days of exposure. The average of individual carbonation depths measured at each point is recorded as carbonation depth of one tested sample. The average 28 days carbonation depth of three replicates in the same group is used as evaluation indicator. Evolution of carbonation depth plotted over time is assessed, but not used as a criterion for comparison between different samples
ISO 1920-12	The carbonation depth of prisms shall be measured after the following exposure periods: 56, 63 and 70 days or as specified after placing in the storage chamber. The carbonation depth of cubes shall be measured at 70 days unless specified otherwise. A slice approximately 50 mm thick shall be broken off the prism after each exposure period and the split surface on the remaining prism resealed to prevent longitudinal carbonation. Where a single determination of the carbonation depth is made on a cube after 70 days of storage, the cube shall be split in half. The depths of carbonation on the freshly broken surface of the split slice shall be measured
	Clear the broken surface immediately of dust and loose particles after breaking, and then spray with a fine mist of indicator solution. Avoid the formation of flow channels on the test surface. If only a weak colouration or none at all appears on the treated surface, spray again after 30 min. The measurements shall be conducted after the colour has stabilised
IS 516 (Part-2/Sec 4) 2021	The carbonation depth of prisms shall be measured after the following exposure periods: 56 days, 63 days, and 70 days or as specified after placing in the storage chamber. The carbonation depth of cubes shall be measured at 70 days unless specified otherwise. Ten single point carbonation depths (dk, point) are measured after each exposure period on each prism or cube and the depth of carbonation dk, is expressed as the mean of the 20 readings
	Clear the broken surface immediately of dust and loose particles after breaking and then spray with a fine mist of indicator solution. Avoid the formation of flow channels on the test surface. If only a weak colouration or none at all appears on the treated surface, spray again after 30 s. The measurements shall be conducted immediately after the colour has stabilized
NT Build 357	After sampling, the specimens are placed inside the compartment, and exposed to the carbonation atmosphere. The carbonation depth is measured at least once a month
RILEM CPC-18	The measured depth of carbonation is influenced by the time of measuring after application of the indicator solution. Therefore, measurements within a series of tests should always be made at the same time. Measuring about 24 h after spraying is recommended, when the margin between carbonated and non-carbonated concrete is often more clearly demonstrated than at earlier measuring times. The precision of the measurement must be to the nearest 0.5 mm. Carbonation depths less than 0.5 mm are not differentiated
SIA 262/1	*Prisms*: In 28 day cured concrete, the zero measurement of the carbonation depth is carried out. After the first measurement (zero measurement), the prism is brought into the rapid carbonation chamber and stored there until the second measurement. The test specimens shall be stored in the accelerated carbonation chamber in a way that ensures unhindered access of air to the exposed surfaces (mutual distance between specimens and distance between specimen and walls > 10 mm)
	After 7, 28 and 63 days the test pieces are removed from the rapid carbonation chamber and the depth of carbonation is measured. For each measurement, an approx. 50 mm thick concrete disk is mechanically split off from the prism (starting from one end face of the prism towards the other end face). Thereafter, the test is continued in the rapid carbonation chamber. The interruption of the accelerated carbonation should be as short as possible (< 1 h). The freshly split-off surface of the concrete disc is first freed of dust and residual material and then sprayed as quickly as possible (< 1 h) with the phenolphthalein solution. After the phenolphthalein solution has dried (a few minutes), the concrete surface is sprayed with the film-forming solution to preserve the color change. Subsequently, the carbonation depth is determined, and the colored concrete disk photographically documented
	Cores: After 3 weeks of storage of the cores in the climatic chamber, the zero measurement of the carbonation depth shall be made. The carbonation depth of one drilled core is determined per time of exposure. For this purpose, this is split in the longitudinal direction and treated in the same manner as the concrete disks. The depth of carbonation shall be measured accurately at 1 mm precision on the cores of 50 mm diameter at 3 points. In cores of $\geq$ 80 mm diameter carbonation should be measured in 5 points in each of the four halves of the cores

Table 5 (continued)

Test	Carbonation reading
UNE 83993-1	After 90 days of exposure, the specimens are split and sprayed with the phenolphthalein indicator. The pH indicator must be applied a few minutes after the samples are split, and well cleaned with a brush. Similar procedure can be followed at other ages

of each phase is not captured by pH indicators, as shown in Fig. 13.

It is worth noting that although all standards include information about how the carbonation front can be determined using a pH indicator, there is only one dedicated standardised testing method for measuring the carbonation depth, EN 14630 [20], whose procedure is similar to that described in EN 12390-12 [18], but provides further details for the carbonation depth determination in large fragments or core samples that may be removed from real structures. RILEM CPC-18 [8] discusses the importance of exposure conditions for inducing carbonation of concrete specimens, but does not provide a specific guideline for exposure of the material, therefore it is often used as a guideline for carbonation depth data collection, and even cited in the BSI 1881-210 and CUR-Aanbeveling 48 standards (Table 5).

Another variation in the standards is the precision level specified for the carbonation depth measurements (Table 5), which is mentioned in very few standards. While most standards establish a precision of 0.5 mm, EN 14630 specifies reporting carbonation depth to the closest millimetre, and ISO 1920-12 requires reporting to a precision of the closest 0.2 mm. These differences will further increase variability in the carbonation depth readings for a given material. The statistical power of the measurements will also differ between standards, with as many as 24 readings (EN 12390-10 with two prisms) collected per time interval for some standards, while others require only 4–5 measurements (Table 5).

Given that changes in the solvent used for preparing the pH indicating solution, as well as the time when the readings are performed, can introduce significant changes in the thickness of the layer experiencing pH changes, there are increased concerns about identifying whether changes in pH can be truly correlated to carbonation of the phase assemblage of a given cementitious system. Consequently,

a variety of methods and approaches have been explored over the past decade. Villain et al. [52] described a methodology to determine carbonation via thermogravimetry, chemical analysis and gamma densimetry. Quantification of portlandite using thermogravimetry has particularly been reported in numerous studies [47, 51, 84, 85]. Van den Heede & De Belie [86] found that the colorimetric carbonation depth obtained through phenolphthalein spraying usually slightly underestimated the microscopically assessed carbonation depth measured on thin sections under crossed polars, both for Portland cement based and for fly ash containing concrete. However, the discussion here of what is truly relevant when measuring carbonation depth depends on whether the main impact of carbonation is considered to be the alteration of the binder mineralogy, or the pH decrease and its consequent effects on corrosion susceptibility. This discussion will depend to a significant extent on the intended engineering usage of the materials and does not appear to have a single definitive answer.

A pH indicator is still the most widely used method for determining the carbonation front, despite the clear evidence that it is uncertain what is being captured by alterations of the pH. Attention has recently been drawn to the fact that phenolphthalein has been identified as carcinogenic [87], and consequently it should be removed from the standards. The standard EN 12390-10 [18] is the only one that specifies the use of an alternative indicator such as thymolphthalein for carbonation assessment. Alternatives such as thymolphthalein, alizarin yellow and rainbow indicators have been successfully used to identify changes in alkalinity in carbonated concrete [54], and so are being more widely adopted in laboratory studies. An added advantage of using such activators is that their colour transitions occur at different pH values from those of phenolphthalein (Table 6), and therefore the colourless regions could be more clearly

associated with specific reactions happening in the binders upon carbonation. A natural pH indicator, curcumin, extracted from commercial turmeric powder and from the rhizomes of the turmeric plant, has proven to be effective in detecting changes in pH in cementitious materials, yielding a red colour in areas where there is an alkaline reserve (pH ~ 12) and yellow in carbonated zones (pH ≤ 9) [88]. Also, natural pH indicators based on anthocyanin extracted from petals of the Chinese violet cress, *Orychophragmus violaceus* [89]*,* grape, red cabbage or black carrot [90] have proven to be effective to identify the pH changes in carbonated concrete. Despite the promising results obtained when using these synthetic and natural pH indicators, as long as the standards continue requiring the use of phenolphthalein, the use of such indicators in practice will continue to be limited.

In recent years, Grengg et al. [91] developed a chemical sensor for high-resolution optical pH imaging of concrete (Fig. 10), providing for the first time 2D visualisation of the pH in a concrete cross section. This is a reliable and highly accurate method that

offers promising advantages for diagnosis of concrete carbonation.

Sakoparnig et al. [92] utilised such optical sensors and compared the changes in pH in carbonated materials with those obtained using a phenolphthalein solution and quantification of portlandite/calcium carbonates (determined by thermogravimetry analysis). Their results demonstrate that 'carbonation depths' determined by the phenolphthalein method do not capture the full conversion of portlandite to calcium carbonate, while the optical sensor does (Fig. 11).

Discrepancies between portlandite consumption, carbonate formation, and pH changes identified by the phenolphthalein method have also been highlighted in other studies [47]. This has been attributed to the gradient of carbonation that will be present in the material (Fig. 12). The formation of a partially carbonated front is known to be controlled by the micro-climate (such as RH level) in the cementitious materials [93] and is often not captured by the phenolphthalein method. This further highlight that the progression of the microstructural

Table 6 pH-value range of colour change of different pH indicating solutions. Reproduced from [83]

Indicator type	pH-value range of colour change
1% phenolphthalein in 70% ethanol	8.2–10 (transparent to fuchsia)
0.1% thymolphthalein in 90% ethanol	9.3–10.5 (transparent to blue)
Rainbow indicator[a]	9–11 (green to purple)
0.5% curcumin in ethanol	7.4–8.6 (yellow to orange)

[a]Ready-mixed indicator from Germann instruments

Fig. 10 pH image of a concrete specimen previously exposed to accelerated carbonation. **A** pH image of the sample, **B** image of the concrete surface used for pH imaging. **C** Combined image of **A** and **B** including reference pH measurements using a flat surface electrode. Reproduced with permission from [91], copyright Elsevier B.V.
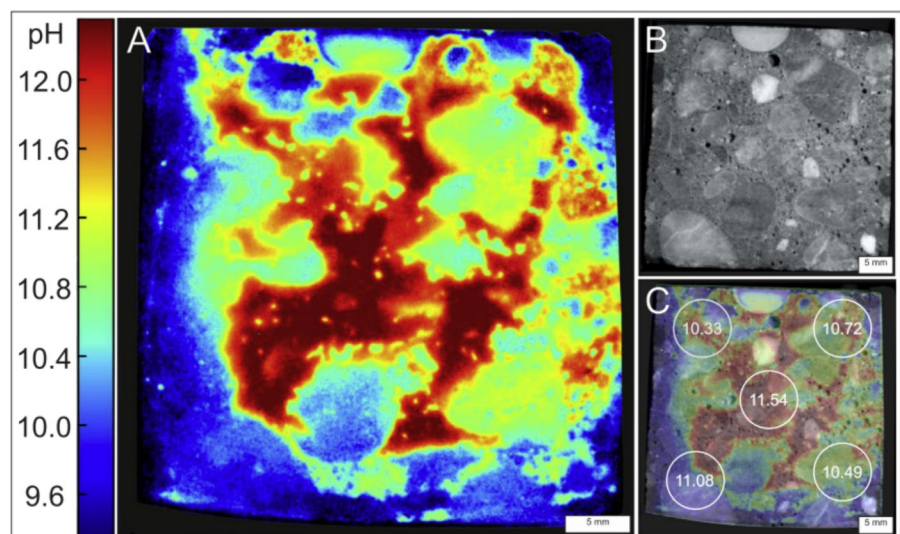
alterations occurring due to the carbonation reaction itself is not fully captured by using a pH indicator.

With the increased use of SCMs in concrete production, the use of a pH indicator for determining carbonation has been extensively questioned, as it is well known that concrete with blended cements will have a lower content of portlandite due to a reduced clinker factor and pozzolanic reaction [94]. In Fig. 13 it is illustrated how the changes in pH are linked to changes in phase assemblage upon carbonation, in blended Portland cements containing calcined clays. A change in pH identified by the phenolphthalein method does not capture the decalcification of Ca-bearing phases (e.g., portlandite/calcium silicate hydrates) or changes in porosity.

In plain Portland cement systems, carbonation is not considered a major durability threat for the concrete per se, as it is known that this phenomenon can lead to densification of the material [95]. Historically carbonation of cement and concrete is of concern when considering its potential impact in the longevity of reinforced concrete structures, linked to the corrosion performance of the steel rebars. It is believed that the reduction in alkalinity of the concrete cover
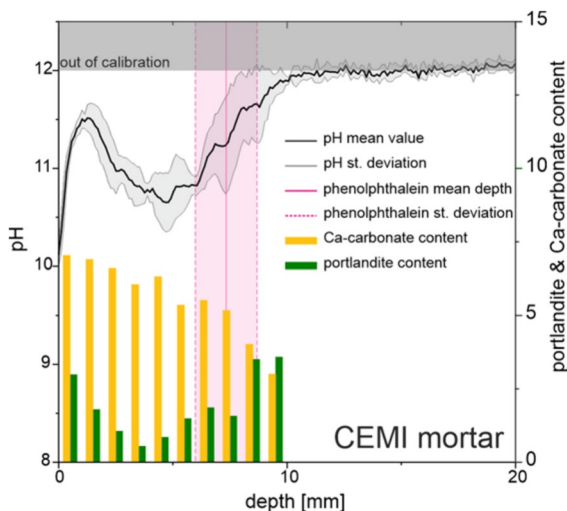

Fig. 12 Schematic of the pH gradient expected in carbonated concrete specimens. Adapted from [93]

layer due to the consumption of portlandite and decalcification of C–S–H during the carbonation process, can lead to the destabilisation/depassivation of the steel reinforcement, and a consequent increase in the risk of failure of concrete structures. A critical analysis of the impact of carbonation on potential corrosion of steel reinforcement, published by Angst et al. [96] within the context of RILEM TC 281-CCC, demonstrated that a reduced pH of the concrete cover

Fig. 11 Comparative results of pH measurements conducted by the phenolphthalein indicator methods vs. an optical sensor, along with quantified contents of portlandite and calcium carbonates determined by thermogravimetric analysis of a Portland cement mortar. The pink region is indicating the carbonation depth measured by the phenolphthalein method, not the range of pH values detected by this method. Courtesy of M. Sakoparnig
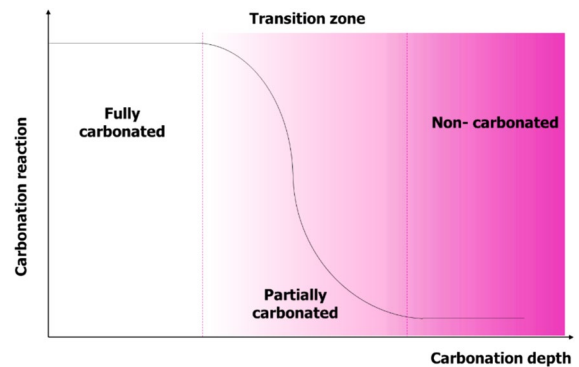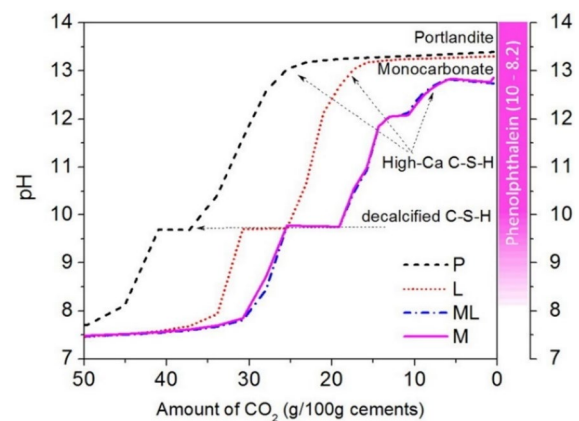

Fig. 13 pH profiles related to the changes in phase assemblages predicted by thermodynamic modelling in blended Portland cement containing calcined clays. The right bar indicates the gradual colour change of phenolphthalein from fuchsia to colourless upon pH changes from 10 to 8.2. *P* corresponds to 100 wt% white Portland cement; *L*—68.1 wt% white Portland cement + 31.9 wt% limestone; *ML* to 68.1 wt% white Portland cement + 25.5 wt% metakaolin + 6.4 wt% limestone; and *M* – 68.1 wt% white Portland cement + 31.9 wt% metakaolin. Reproduced with permission from [35], copyright Elsevier B.V

layer alone is not sufficient to lead to significant corrosion of steel rebars in concrete. It is important to stress that assuming that concrete carbonation will automatically lead to corrosion of steel in reinforced concrete is a simplification of the mechanism of corrosion of the steel reinforcement, as there is no consistent evidence in concrete structures that carbonation of concrete will lead to corrosion. Other factors such as pore structure, moisture content, and composition of the pore solution at the steel–concrete interface, will influence how and to what extent carbonation-induced corrosion of the steel reinforcement will proceed [97].

6 Natural versus accelerated carbonation

6.1 Natural carbonation exposure

Several standards (e.g. CUR-Aanbeveling 48:2010, NT Build 357, RILEM CPC-18, UNE 83993 – 1: 2013) mention how and/or how often the reading of carbonation depths in concrete specimens can be performed using the phenolphthalein indicator and how results can be reported, when specimens are exposed to natural carbonation conditions. The environmental conditions (RH, T and CO_2 concentration) must be collected periodically and reported along with the carbonation rates.

EN 12390-10 is the only available standard that provides detailed information about how to care for samples exposed to natural carbonation in different climatic conditions (e.g. indoor natural environment, indoor controlled environment, outdoor sheltered or outdoor unsheltered). Additionally, it prescribes the conditions to be applied in a climate-controlled chamber if it is used to simulate an indoor environment. In such cases, relative humidity (RH) and CO_2 concentration must be recorded at least once every two hours. The average for the CO_2 concentration over the test duration should be $(0.040 \pm 0.001)\%$ by volume with no variation outside $(0.040 \pm 0.005)\%$, and the RH should be $(65 \pm 2)\%$. Temperature must be measured at least once per day at a constant time, and remain in the range (20 ± 2) °C. Results from the RILEM TC 281-CCC interlaboratory test show that although temperature and RH are usually well controlled, none of the climatic chambers used by the different laboratories were able to comply with the specific CO_2 value ranges required by the standard [5]. This demonstrates that even under controlled environments, variations in the exposure conditions will occur.

6.2 Natural versus accelerated carbonation

General information about service life prediction models that account for carbonation of concrete can be found in Alexander et al. [98], where a critical state of the art review about durability, service life prediction and modelling for reinforced concrete structures is reported. It is not the objective of the present analysis to revisit such studies. Instead, we intend to create awareness about the current approaches in using accelerated carbonation results from standardised testing methods, attempting to correlate natural and accelerated carbonation not just with the intention of predicting concrete durability, but also attempting to quantify the CO_2 uptake capacity of concrete.

Many studies and reviews have been published correlating accelerated and natural carbonation results of concrete including [14, 15, 40, 99], just to mention a few. Also within the framework of RILEM TC 281-CCC an extensive interlaboratory test campaign was performed to compare natural carbonation of mortar and concrete with CEM I, CEM II/B-V and CEM III/B, and to investigate its relationship to accelerated carbonation [5]. Often, accelerated carbonation results are used to develop models which are included in codes and standards such as the *fib* Model Codes (e.g. *fib* MC 2010, Bulletin 34 Model code for service life design [100]) and ISO 13823:2008 [101] with the aim of predicting service life performance, and/or to aid the design of concretes accounting for their potential durability [102].

Despite the extensive scientific evidence that carbonation of cementitious materials is both a chemical reaction and a diffusion-controlled mechanism, particularly for concrete with SCMs [2], a direct correlation between natural and accelerated carbonation results is generally made according to Eq. (1). This equation is derived from the assumption that carbonation is only a diffusion-controlled mechanism, and therefore can be described by Fick's first law of diffusion. According to Eq. (1), there is a direct correlation between the carbonation coefficient (k_c) and the concentration of CO_2 under natural ($c_{CO2, \, nat}$) or accelerated ($c_{CO2, \, acc}$) carbonation exposure conditions [103].

$$\frac{k_{\text{c-acc}}}{k_{\text{c-nat}}} = \sqrt{\frac{c_{\text{CO2, acc}}}{c_{\text{CO2, nat}}}} \qquad (1)$$

Such a relationship is well accepted, and it has been extensively used for correlating natural and accelerated carbonation results. However, this relationship is only valid if the degrees of saturation of the concrete and the maturity of the binding phase (concrete matrix) are comparable at the moment of testing, so the mechanism of carbonation under different exposure conditions is comparable. It is worth noting that the *fib* model code as well as in the SIA standard include empirically determined correcting factors or equations to account for the differences in carbonation kinetics and material age influencing the calculated carbonation rates when using natural or accelerated carbonation data.

This important aspect is often overlooked, as it is impossible to simulate, under accelerated carbonation conditions, all the variety of climates at which natural carbonation assessment is conducted. Consequently, Eq. (1) is often directly applied to draw conclusions about natural or accelerated carbonation performance. It is well documented in literature that this equation is not valid for converting carbonation rates obtained at a certain CO_2 concentration to another one, even for situations where the temperature and RH are virtually the same. Figure 14 shows data of Van den Heede [104] where the carbonation coefficients corresponding with exposure to 10% CO_2 were implemented in this equation to estimate a carbonation coefficient for a 1% CO_2 environment.

If Eq. (1) held, then the estimated carbonation coefficient for 1% CO_2 should not differ too much from the measured value. This was clearly not the case, as for both mixtures F(1)50 with 50% fly ash in the binder and for the PC reference T(0.55), the estimated values (bold line) were only 55% and 38% of the measured values. One possible explanation for this underestimation of carbonation rates when testing at high CO_2 concentrations and using Eq. (1) for conversion, is the excessive production of water during carbonation at 10% CO_2 which induces pore blocking. Van den Heede et al. [76] further investigated this phenomenon for high-volume fly ash (HVFA) mortars with 50% PC and 50% fly ash via carbonation tests at $\pm 0.04\%$ CO_2 (natural carbonation), 1% CO_2 and 10% CO_2. Internal humidity sensor monitoring and ^{1}H NMR relaxometry revealed the highest water vapour and liquid water contents after carbonation at 10% CO_2 (Fig. 15) [76].

7 Beyond durability assessment

Carbonation coefficients determined via extensive experimentation are included in some standards such as EN 16757:2022 '*Sustainability of construction works. Environmental Products Declarations*' [105], and the related document PD CEN/TR 17310:2019 '*Carbonation and CO_2 uptake in concrete*' [106]. Tables reporting carbonation coefficient values are explicitly given as a function of the concrete strength class, along with a table for correcting such carbonation coefficients for concrete containing SCMs

Fig. 14 Effect of the applied CO_2 concentration on the carbonation coefficient of mixtures (**a**) with 50% fly ash in the binder and (**c**) a PC reference with w/c ratio of 0.55; measured values are shown by markers, calculated values for 1% CO_2 based on Eq. (1) by the bold line. Courtesy of P. Van den Heede
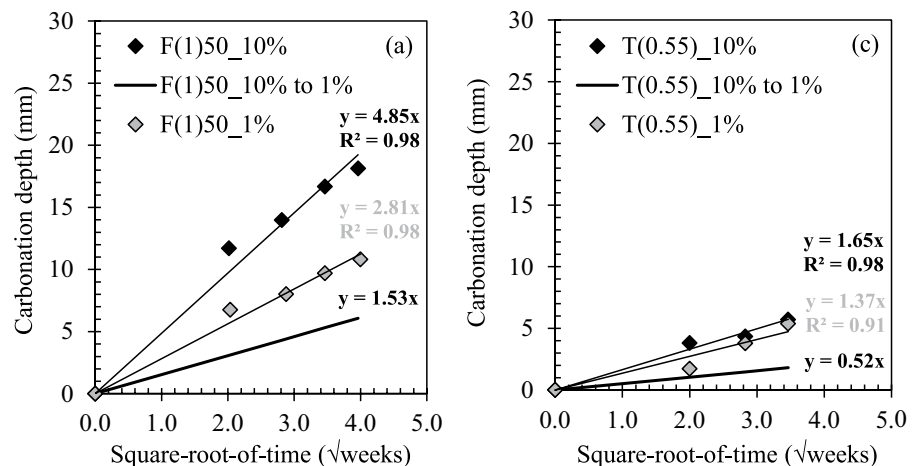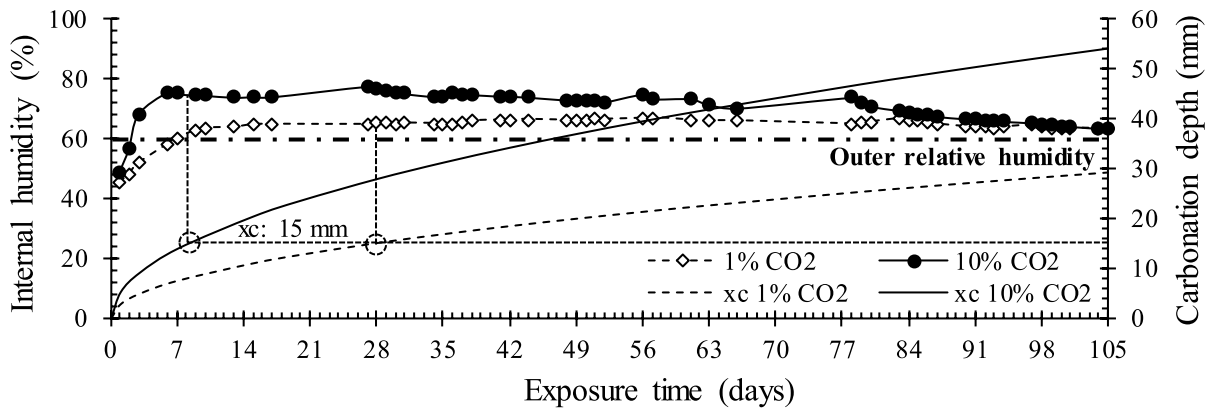
Fig. 15 Evolution of the internal humidity measured with humidity sensors at a depth of 15 mm during carbonation at 1% CO_2, 20 °C, 60% RH and 10% CO_2, 20 °C, 60% RH in (limited to limestone, silica fume, fly ash and blast furnace slag). As the carbonation coefficient varies as a function of the time and environmental exposure conditions, using a single or average value to describe the performance of concrete accounting solely for their compressive strength is not an accurate representation of the processes that take place under real-world conditions, but is a simplification that is easy to use in practical engineering applications.

high volume fly ash (HVFA) mortars, with indication of when the carbonation depth reached 15 mm. Reproduced with permission from [76], copyright Elsevier B.V

The same simplified approach to approximate the carbonation rates of different concrete has been used in previous estimates of the CO_2 uptake (re-carbonation) of concrete in Northern Europe [107] and globally [108]. The carbonation rates used in these studies and the above-mentioned standards derive from early, seminal reports, which provided a first collation of recommended values to be used for k_c to estimate the CO_2 uptake by cementitious materials during lifetime and after demolition [109, 110]. However, these reports were prepared about two decades ago, and significant new developments have occurred in cement technology, yielding to extensive new data and insights into the carbonation process. The reports themselves advised that the values will be revised when sufficient new data is available.

In this context, it is imperative to harmonise standards for determining carbonation performance of concrete, to ensure that the different carbonation coefficient values reported in the literature are comparable and can have some validity in service life prediction models or re-carbonation calculations. As highlighted in Sect. 3, the limited accuracy of the pH indicator method for revealing carbonation progress opens the

question of how reliable it is as a method to establish (up to a certain extent) the sustainability credentials of cement, concrete or structures using carbonation coefficients determined via this method. As discussed throughout this critical overview, there are other testing parameters that introduce significant variability in the results, when adopting different standardised testing methods. Therefore, it is uncertain which carbonation results can be deemed correct for CO_2 uptake potential calculations, because in a practical sense, as long as the data are obtained according to a standardised testing methodology, it will be accepted as representative of a given material.

8 Concluding remarks

Carbonation is one of the major durability threats of modern blended Portland cement systems. Despite the extensive knowledge gained over the past decades about this phenomenon, there is a lack of consensus about how carbonation of concrete needs to be evaluated, as evidenced by the fact that many standardised testing methodologies can be applied for this purpose. There are notable differences among existing standardised testing methods that will introduce variability of the results. Therefore, accelerated carbonation testing methods should be considered only to distinguish carbonation performance among concretes tested under comparable conditions.

The sample pre-conditioning and curing will influence the maturity of the binding phase, and consequently its response to CO_2 exposure. The

incorporation of a maturity index within methodologies for evaluating durability of concrete with SCMs is urgently needed, and should be prioritised in future iterations of standards, so that concrete longevity can be determined more accurately. Accelerated carbonation exposure conditions influence the carbonation mechanism and the extent of changes the material will experience. A consensus needs to be reached about exposure conditions to be adopted across different standards, particularly defining the CO_2 concentration and relative humidity for testing. For Portland cement and blended Portland cements it seems that 1 to 3% CO_2 concentration is adequate for inducing comparable phase assemblage changes to those identified during natural carbonation exposures. Therefore, testing accelerated carbonation of concrete at CO_2 exposure concentrations beyond this value is not recommended. It is important to promote the harmonisation of this parameter across existing standards to enable more direct comparisons between results from different studies, to increase the understanding of how the intrinsic properties of individual concrete can be linked to their carbonation resistance.

There is still need for research to translate carbonation rates obtained via accelerated tests accurately to carbonation rates under natural conditions for different types of concrete. Concrete with SCMs will undergo different microstructural changes due to carbonation than ordinary Portland cement concrete (often coarsening instead of refinement of the pore structure). Exposing these concretes to high concentrations of CO_2 will lead to rapid carbonation, which in turn can lead to higher production of water internally (as a reactant of the carbonation reaction). The differences in water release upon carbonation might also influence the RH conditions at which the carbonation rate will be higher.

Carbonation of concrete has been historically linked to a reduction of the pH, which is determined using a phenolphthalein solution. The analysis performed in this paper has led to two conclusions related to this premise: (i) the use of this carcinogenic substance could be removed from existing standards, and alternative synthetic or natural pH indicators need to be recommended instead; (ii) the use of a pH indicator does not fully capture the carbonation reactions taking place in concrete. For Portland cement concrete, it can be argued that changes in alkalinity induced by carbonation are of relevance in

the context of steel corrosion. For blended Portland cement concrete, carbonation can lead to a reduced loading capacity and increased porosity of the material, so independent of the changes in alkalinity that can be associated with carbonation, it is of relevance to determine the extent of microstructural changes carbonation has induced, which the pH indicator method is failing to reveal. The limited accuracy of the methodologies used for determining carbonation depths calls for selection of suitable approaches to answer the questions raised when planning such experiments. Carbonation coefficients determined from carbonation depth readings using the pH indicator method might not be truly representative of the actual carbonation the material is experiencing. This is concerning for service life prediction models, particularly for concrete with SCMs.

The oversimplified recommendations that are in place to calculate CO_2 uptake by concrete using standards originally developed for accelerated carbonation rate determination, and consequently define the sustainability credentials of cements, concrete or structures assuming constant carbonation coefficient values, are potentially misleading at a technical level. The carbonation coefficients estimated from carbonation depth results determined according to the different standardised testing methodologies are imprecise, and unique to individual concrete mix designs and environmental exposure conditions. Often no direct correlation between carbonation coefficient and compressive strength is identified in concrete with SCMs, particularly when performance is determined under accelerated testing conditions. Therefore, such recommendations based on using carbonation coefficients tabulated in such standards need to be questioned.

Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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