

# An analysis of existing models for carbonation coefficient applied to tests under natural conditions

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## Abstract

The carbonation exposure classes adopted by EN 206 enforce minimum cement contents for concrete mix design, therefore placing limits on achievable embodied carbon. Understanding the mechanisms behind carbonation of concrete structures would allow for more accurate specification of appropriately durable concretes, without overspecification of cement content. Various models for concrete carbonation exist in the literature, and these are grouped into: strength based, stoichiometric, microstructural, and empirical models. Examples of each class of model for concrete carbonation are compared against published data from natural carbonation tests to assess their accuracy and driving factors of carbonation resistance. The selected models are able to capture the general trends of the data with some reliability. However, the precision and accuracy of the estimates are low. It is possible that this loss of accuracy is a result of differences in the carbonation mechanism in accelerated carbonation tests, upon which the predicted models are typically calibrated, and natural carbonation processes, for which estimates are required to predict the response of real-world structures.

*Keywords: Carbonation, durability, modelling, performance-based design.*

## 1. Introduction

Concrete carbonation describes the process of atmospheric CO<sub>2</sub> reacting with hydration products in concrete, such as calcium hydroxide (Ca(OH)<sub>2</sub>) and calcium silicate hydrate (3CaO·2SiO<sub>2</sub>·3H<sub>2</sub>O). This leads to a reduction in the pH value of the concrete and loss of passivation of encased steel reinforcement. The carbonation process is often modelled by Fick's first law of diffusion, where the carbonation distance,  $x_c$ , is proportional to the square root of time,  $t$ , through a constant carbonation coefficient,  $K$ :

$$x_c = K\sqrt{t} \quad (1)$$

The assumption is made that the carbonation reaction is much faster than the diffusion of CO<sub>2</sub> through the concrete, so the overall carbonation rate is diffusion controlled (Chatterji, Snyder and Marchand, 2002).

The carbonation coefficient should capture the influence of many different material properties and environmental conditions for an analytical carbonation model to be accurate. In this work, existing models to determine the carbonation coefficient are considered and compared to published data for the carbonation of concrete specimens under natural carbonation (NC) conditions. NC tests are carried out at atmospheric CO<sub>2</sub> concentrations, with all other conditions such as relative humidity (RH) and temperature being controlled.

Current design practice in EN 206 (British Standards Institution (BSI), 2016) dictates a minimum cement content, minimum compressive strength, a maximum water/cement ( $w/c$ ) ratio and acceptable cement designations for concretes to satisfy particular carbonation exposure classes. This is consistent with the common assumption that the rate of carbonation of Ordinary Portland Cement (OPC) concretes is influenced primarily by their water/cement ( $w/c$ ) ratio (Basheer, Russell and Rankin, 1999), which also primarily influences compressive strength (Mohammed Abas Abdela Salem, 2015). However, this

potentially does not capture the influence of other factors in the mix design and casting process on the carbonation performance of the resulting concrete.

Furthermore, due to a desire to reduce the embodied carbon of concretes, there is increasing interest in using cements which are rich in supplementary cementitious materials (SCMs). Therefore, how their carbonation performance differs from OPC concretes of the same mix parameters is of interest. When SCM additions are present,  $w/c$  may be replaced with  $w/c_{eqv.}$  using the k-value concept in EN 206 (BSI, 2016), where  $w/c_{eqv.} = \text{water}/(\text{cement} + k \times \text{addition})$  and  $k$  is the efficiency factor of the SCM. This differs from the water/binder ratio ( $w/b$ ), where  $w/b = \text{water}/(\text{cement} + \text{addition})$ .

A performance driven approach to carbonation may allow lower volumes of cementitious materials and different blended cements to be used without jeopardising long term durability, thereby reducing embodied carbon emissions. Understanding carbonation mechanisms to promote a performance driven approach is therefore of great importance to improving cement efficiency.

## 2. Method

### 2.1. Existing analytical carbonation models

Many analytical models to find the carbonation depth,  $x_c$ , are proposed within the literature. Summaries of some existing models are presented by Qiu (2020) and Zhou *et al.* (2015). The gathered carbonation models are generally generated empirically by comparing influencing factors to experimental data. The model equations in principle follow Fick's law, given by equation 1, but differ in their calculation of the carbonation coefficient,  $K$ . Further analysis shows these models may generally be categorised into the four following categories:

- **Strength based models:** these models assume that greater strength concretes will exhibit greater carbonation resistance as mechanisms for improving strength also improve durability characteristics.
- **Stoichiometric models:** these models use information about the stoichiometry of the carbonation reaction and the chemical composition of the mix constituents to determine the expected depth of carbonation.
- **Microstructural models:** these models assume that the rate of carbonation is determined by the impedance of diffusion of carbon dioxide resulting from the microstructure only, and therefore include a microstructural property such as gas permeability or porosity in their formulation.
- **Empirical diffusion models:** these models are calculated based on properties measured from the same concrete in an accelerated carbonation test.

One analytical model from each category is applied in this work. These are summarised in Table 1.

Table 1. Carbonation models assessed

Model type	Source	Model inputs
Strength	<i>fib</i> model code 2010, initial estimate value ( <i>fib</i> , 2012b)	Compressive strength, CO <sub>2</sub> concentration
Stoichiometric	Papadakis, (2000)	Mix proportions, Chemical composition of cement, CO <sub>2</sub> concentration, Relative humidity
Microstructural	Zhang <i>et al.</i> , (2013)	Gas permeability coefficient, Relative humidity, CO <sub>2</sub> concentration
Empirical	<i>fib</i> bulletin 34 ( <i>fib</i> , 2006)	$w/c_{eqv.}$ ratio, Relative humidity, CO <sub>2</sub> concentration, curing period

### 2.2. Validation of analytical carbonation models

To assess the accuracy of the four collated models as predictive tools for carbonation performance, the models are assessed against a total of 62 concrete specimens tested in natural carbonation conditions

and retrieved from literature sources (Balayssac, Détriché and Grandet, 1995; Parrott, 1996; Sanjuán, Andrade and Cheyrezy, 2003; Ribeiro, Santos and Gonçalves, 2018).

### 2.2.1. Assumptions and input parameters

Some of the models require the results of material characterisation tests or additional assumptions to be used as predictive tools. Where compressive strength was not given it has been calculated using relationships described in the BRE mix design method (Marsh *et al.*, 1997), using appropriate assumptions and published properties of mix constituents where available. Where cylinder compressive strengths are required,  $f_{cyl} = 0.8 \times f_{cube}$  is assumed, consistent with the *fib* Model code 2010 for concretes below 60 MPa (Fédération Internationale du Béton (*fib*), 2012a). Where gas permeability values are required, these are estimated using the *fib* model code 2010 expression (*fib*, 2012a):

$$K_g = \frac{2 \times 10^{-10}}{(f_{cyl,m})^4} [\text{m}^2] \quad (2)$$

where  $f_{cyl,m}$  is the mean compressive cylinder strength in MPa.

For stoichiometric models, the chemical composition of all the cementitious materials present in a sample are required to calculate the amount of carbonatable material. A variety of cementitious materials are included in the test data, with compositions including CEM I or CEM II/A-L and various SCMs: Silica Fume (SF), High-calcium Fly Ash (FH), Low-calcium Fly Ash (FL) Ground Slag (GGBS) and Limestone (LS). Where chemical information is not provided alongside carbonation results in the original publications, the values in Table 2 are assumed. The chemical composition of LS is not required since the overall composition of the blended limestone cement used by Balayssac, Détriché and Grandet (1995) is known. The efficiency factors (k-values) for each SCM are also given in Table 2, obtained from EN 206 (BSI, 2016). The k-value for LS is taken as 0.5 (Kim *et al.*, 2018).

Table 2. Assumed physical and chemical characteristics of common cementitious materials, from (Papadakis, 2000; Ribeiro, Santos and Gonçalves, 2018)

	CEM I	CEM II/A-L	SF	FL	FH	GGBS
Physical properties						
Density	3130	3130	2260	2250	2660	2880
Glass phase (%)	-	-	96	75	50	50
Chemical analysis (%)						
SiO <sub>2</sub>	18.38	17.30	90.90	53.50	39.21	38.67
Al <sub>2</sub> O <sub>3</sub>	5.23	4.98	1.12	20.40	16.22	9.98
Fe <sub>2</sub> O <sub>3</sub>	3.48	3.16	1.46	8.66	6.58	1.26
CaO	64.02	62.56	0.69	3.38	22.78	37.82
SO <sub>3</sub>	2.83	2.72	0.38	0.60	4.30	0.62
Other	6.06	9.28	5.45	13.46	10.91	11.65
Efficiency factor, k	-	-	2.0	0.4	0.4	0.6

In some sources the exact mix composition is not listed (Balayssac, Détriché and Grandet, 1995; Parrott, 1996), but ratios such as  $w/b$ , aggregate/binder ( $a/b$ ) and sand/aggregate ( $s/a$ ) are provided instead. In these cases, an approximation of the mix composition can be made by assuming an overall concrete density of 2400 kg/m<sup>3</sup>.

### 2.2.2. Experimental data from literature

Some basic information about the concretes selected for analysis is given in Table 3. Mixes with 28 day curing periods were selected for consistency across the different sources. A blended cement with 25% limestone is used by Balayssac, Détriché and Grandet (1995). In all other sources, varying quantities of SCM additions are combined with CEM I or CEM II/A to produce a wide variety of broad designations (i.e. CEM II/B, CEM III/A).

Table 3. Summary of mix designs collected from literature.

Source	No. of specimens	w/b ratio	w/c <sub>eqv</sub> ratio	a/b ratio	SCMs investigated	f <sub>cube,28 days</sub> (MPa)
Sanjuán, Andrade and Cheyrezy (2003)	8	0.33 - 0.69	0.33-0.69	4.8 - 8.0	SF, FL, FH	17.0 - 58.0
Parrott (1996)	17	0.59	0.59-0.89	5.9	GGBS, LS	25.5 - 45.7
Balayssac, Détriché and Grandet (1995)	4	0.48 - 0.65	0.55-0.74	4.2 - 6.4	LS	25.1 - 43.5
Ribeiro, Santos and Gonçalves (2018)	33	0.34 - 0.65	0.34-1.18	4.1 - 7.7	FA, GGBS	16.0 - 84.3

The experimental conditions of the original experiments are summarised in Table 4.

Table 4. Test conditions of data collected from literature.

Source	RH (%)	Conc. CO <sub>2</sub> (%)	Test duration
Sanjuán, Andrade and Cheyrezy (2003)	50	0.03	2 years
Parrott (1996)	60	0.04	18 months
Balayssac, Détriché and Grandet (1995)	60	0.03	18 months
Ribeiro, Santos and Gonçalves (2018)	55-85 (70 assumed)	0.005 - 0.015 (0.01 assumed)	10 years

### 3. Analysis

#### 3.1. Experimental carbonation coefficients

The experimental carbonation coefficient,  $K_{\text{measured}}$ , is obtained for each of the carbonation test results using the published carbonation depths and equation 1. Where multiple datapoints are published for the same concrete mix, a linear least squares regression is used to obtain a more robust value of  $K_{\text{measured}}$ .

Values of  $K_{\text{measured}}$  are plotted against concrete cube strength in Figure 1, w/c<sub>eqv</sub> in Figure 2, and total cementitious binder content in Figure 3. These variables are of importance as they are inputs into many of the analytical models, but also form the basis for decisions about carbonation classification in EN 206 (BSI, 2016).

Plotting measured carbonation coefficients against compressive strength (Figure 1) demonstrates that there is a negative correlation between compressive strength and carbonation coefficient, such that generally stronger concretes display better carbonation resistance. This is consistent with the assumptions of strength-based models and the current practice of specifying higher strengths for better durability performance.

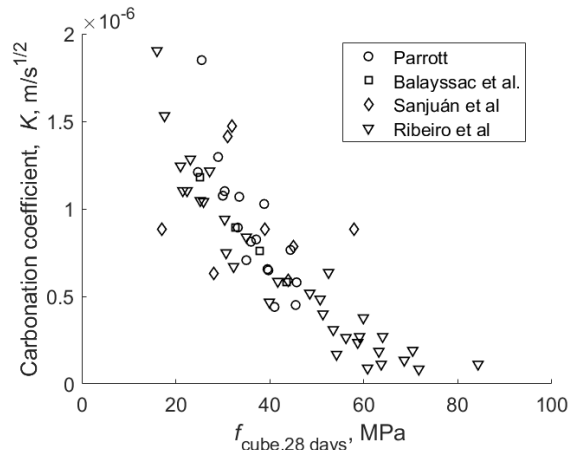


Figure 1. Compressive strength compared to measured carbonation coefficients from natural carbonation tests

The  $w/c_{eqv}$  ratio shows a positive but weak correlation with carbonation coefficient in Figure 2(a), suggesting that this is not the only factor of the concrete mix design affecting carbonation performance. For any given  $w/c_{eqv}$  ratio, a wide range of carbonation resistances are observed. This implies that  $w/c_{eqv}$  ratio cannot be used as a sole indicator of carbonation performance, particularly when SCMs are involved. Ribeiro, Santos and Gonçalves (2018) found that the water/clinker ratio gave a better correlation with carbonation depth. However, this is plotted in Figure 2(b) and shows no improvement in correlation compared to Figure 2(a). The clinker content is taken as 92.8% of CEM I or 84.2% of CEM II/A-L cements (Ribeiro, Santos and Gonçalves, 2018). The cement used by Balayssac, Détriché and Grandet (1995) is 75% clinker.

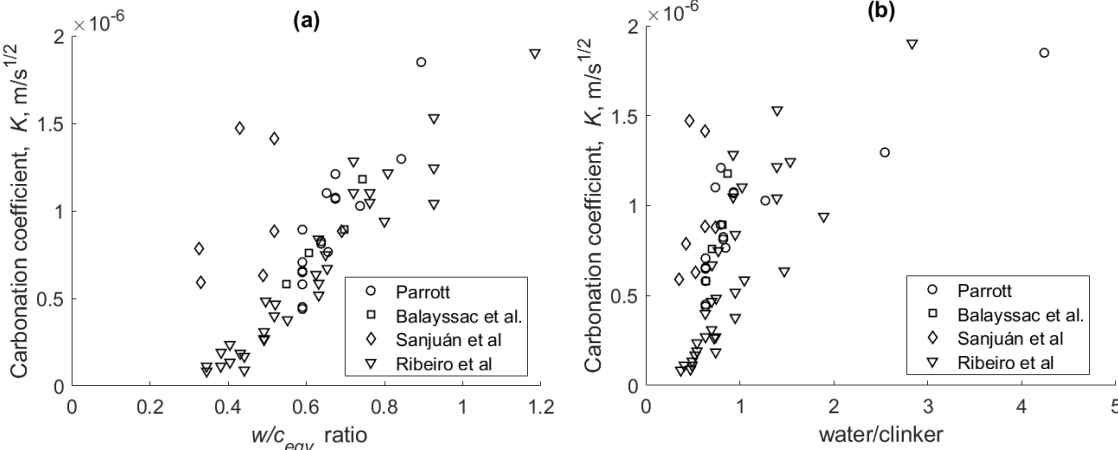


Figure 2 (a)  $w/c_{eqv}$  ratio and (b) water/clinker ratio compared to measured carbonation coefficients from natural carbonation tests in the literature.

Figure 3(a) shows a weak negative correlation between total binder content and carbonation depth. This is slightly improved by plotting carbonation coefficient vs equivalent cement content using the k-value concept, where  $c_{eqv} = cement + k \times addition$  (Figure 3(b)), but there is still a large range of possible values of  $K$  for a given amount of cement equivalent. It is therefore likely that defining a minimum cement content is not always an effective means to define the carbonation performance of a concrete mix; in Figure 3(a), some mixes with 435  $kg/m^3$  of cementitious material performed the same against carbonation as others with lower 320 or 250  $kg/m^3$  contents of cementitious material.

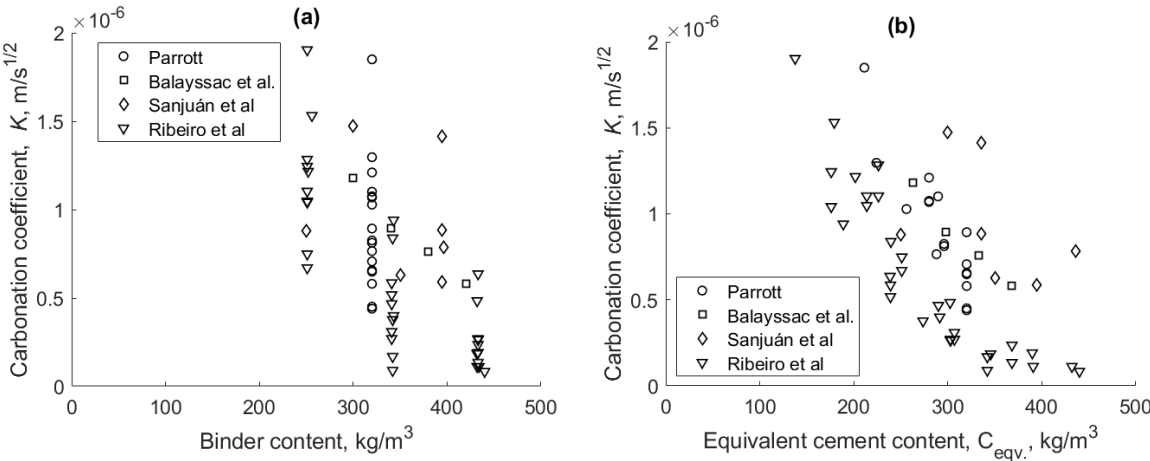


Figure 3. Measured carbonation coefficients compared to (a) total binder content, and (b) equivalent cement content

### 3.2. Model performance

The measured values of carbonation coefficient,  $K_{\text{measured}}$ , are compared in Figure 4 to estimates,  $K_{\text{predicted}}$ , calculated using each of the analytical models. The statistical performance metrics described below are also indicated on the plots.

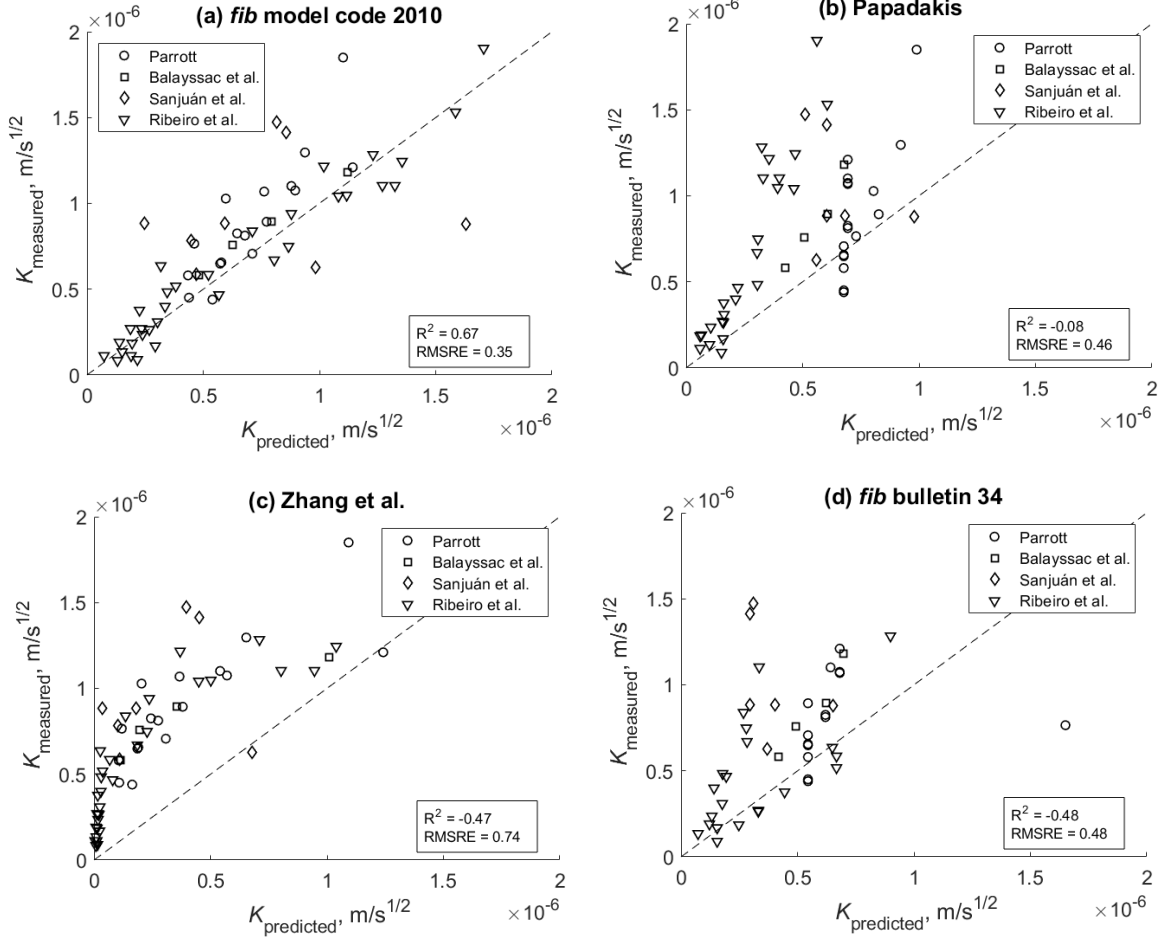


Figure 4. Predicted vs measured carbonation coefficients for a range of concretes under natural carbonation test conditions. Predicted values calculated using models from (a) *fib* model code 2010, (b) Papadakis, (c) Zhang *et al.* and (d) *fib* bulletin 34

#### 3.2.1. Statistical metrics

Statistical metrics are used to evaluate the performance of each of the 4 models against the measured dataset. In particular, the coefficient of determination,  $R^2$ , and root mean square relative error, RMSRE, are calculated using equations 3 and 4. Advantages and disadvantages of these goodness-of-fit metrics are summarised by Despotovic *et al.* (2016).

The coefficient of determination, also known as the  $R^2$  statistic, is an indication of the goodness of fit of a linear regression model to data, in this case the model is  $K_{\text{measured}} = K_{\text{predicted}}$ . A coefficient close to 1 indicates that the model describes the data well (assuming Fickian diffusion holds), whereas a coefficient less than 0 implies that the model cannot explain the variation in the data any better than a prediction equal to the average measured value (i.e.  $K_{\text{measured}} = \bar{K}_{\text{measured},i} = \frac{1}{N} \sum_{i=1}^N K_{\text{measured},i}$ ).

$$R^2 = 1 - \frac{\sum_{i=1}^N e_i^2}{\sum_{i=1}^N (K_{\text{measured},i} - \bar{K}_{\text{measured},i})^2} \quad (3)$$

The RMSRE is adopted as an indicator of root mean square relative error; a measure of the error in the predictions relative to the measured values.

$$\text{RMSRE} = \sqrt{\frac{1}{N} \sum_{i=1}^N \frac{e_i^2}{K_{\text{measured},i}^2}} \quad (4)$$

where  $N$  = total number of datapoints. Note that some of the models have limitations on their validity, for example  $w/c_{\text{eqv}}$  ratio constraints, so do not generate estimates for all specimens and therefore in some cases  $N < 62$ .

The  $R^2$  statistics for three of the models are negative, suggesting there is large variation in the results which is not explained by any of these models.

This analysis suggests that the most accurate model for the spread of natural carbonation test results is the *fib* model code 2010 initial estimate. With an overall  $R^2$  value of 0.67, and a RMSRE of 0.35, this model is not highly accurate but is more consistent with the selected data than the other models. The Zhang *et al.* model appears the least accurate based on RMSRE. However, with the poorest  $R^2$  statistic, the variability in the data is least well explained by the *fib* bulletin 34 model.

Despite the statistically poor performance, all the models make predictions within an order of magnitude accuracy. For a phenomenon as complex as carbonation this may be considered some success.

### 3.2.2. Range of error

The mean and interquartile range of the relative error for the predictions from each of the models can determine whether a model consistently over or under predicts the carbonation coefficient. Outliers in Figure 5 are indicated by crosses. In this work, error is defined as  $e = K_{\text{predicted}} - K_{\text{measured}}$ , such that negative error is an indication of underprediction. Relative error is proportional to the measured value  $e_{\text{relative}} = \frac{K_{\text{predicted}}}{K_{\text{measured}}} - 1$ .

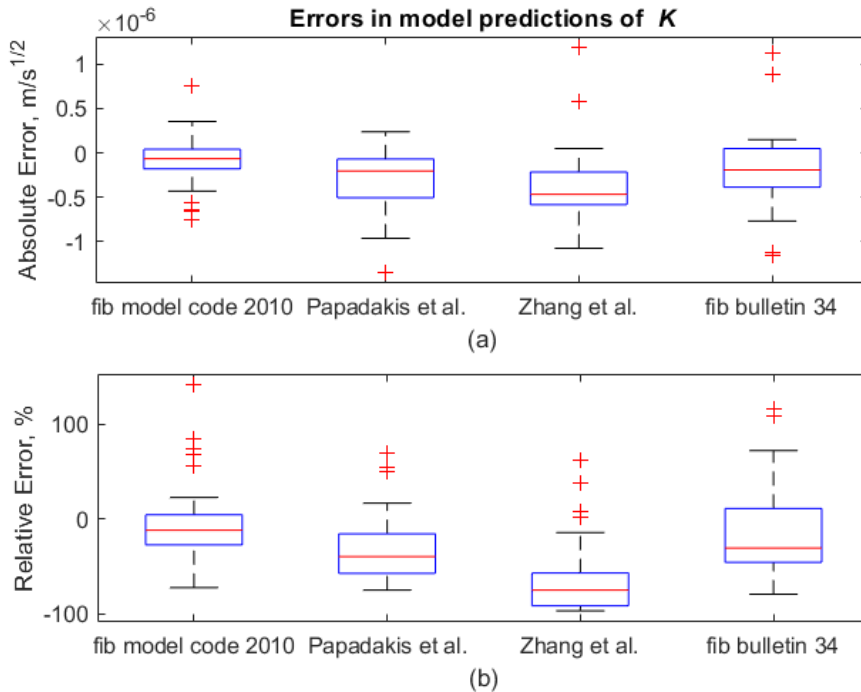


Figure 5. Error in models when compared to natural carbonation test results. (a) absolute error and (b) relative error values

Figure 5 demonstrates that all four models are more likely to underpredict than overpredict the overall carbonation coefficient, with even the most accurate *fib* model code 2010 model giving a median underprediction of 11.8% in Figure 5 (b). This is concerning, as it would lead to underprediction of carbonation depth and therefore potentially undetected damage if exposed concrete in a real structure behaved as the tests indicate. However, at atmospheric CO<sub>2</sub> concentrations, natural carbonation tests use optimal RH and temperature concentrations to promote a steady rate of carbonation, which are unlikely to be seen in real world conditions. Real structures are also likely to have some protective coating or cladding preventing air access, which further reduces the likelihood of severe carbonation.

### 3.2.3. Impact of test conditions

Most of the literature models include a term for the concentration of CO<sub>2</sub> such that  $K \propto \sqrt{CO_2}$ , and the *fib* bulletin 34 model includes a term for directly converting between natural and accelerated carbonation conditions. This would imply that the results of natural carbonation tests (~0.04% CO<sub>2</sub>) and accelerated carbonation tests (2-100% CO<sub>2</sub>) are comparable. The majority of analytical models for carbonation are developed from accelerated carbonation tests, as these produce measurable carbonation depths in reasonable time frames. However, studies comparing natural and accelerated test results (Sanjuán, Andrade and Cheyrezy, 2003; Neves, Branco and De Brito, 2013) suggest that the factor of increase in carbonation rate under accelerated conditions is not strictly proportional to the square root of the factor of increase of CO<sub>2</sub> concentration. This discrepancy may be due to differences in which compounds are able to carbonate at different concentrations (Auroy *et al.*, 2018), meaning that accelerated carbonation is a different chemical process to natural carbonation and direct comparisons are not reliable (Van Den Heede, De Schepper and De Belie, 2019).

Nonetheless, accelerated carbonation continues to be a key method used to develop models for the carbonation response of real structures. Accelerated carbonation tests are known to have been used to develop at least three of the four models investigated in this work (Papadakis, 2000; *fib*, 2006; Zhang *et al.*, 2013), and therefore the performance of these models may be in part be attributed to discrepancies between accelerated and natural conditions.

### 3.2.4. Data validation

The initial estimate model presented in the *fib* model code 2010 is intended as a rough guide, with the same document providing a recommendation to use the *fib* bulletin 34 statistical model for a more accurate estimate of the probability of failure. However, the *fib* bulletin 34 model requires input from preliminary accelerated carbonation tests, which may not be available in all cases. The recommended preliminary test values from the *fib* bulletin 34 (based simply on  $w/c_{eqv}$  ratio and cement designation) for use in the absence of primary data were adopted in this analysis. Given the comparison between Figures 4(a) and 4(d) it appears that, in the absence of primary data, the initial estimate from the *fib* model code 2010 based on strength gives a more accurate estimate than that obtained using the *fib* bulletin 34 and its provided data. This may be because, as indicated by Figure 2, the  $w/c_{eqv}$  ratio was not strongly correlated to carbonation coefficient for the experimental data used here. This suggests that other inputs are required to estimate resistance, and the *fib* bulletin 34 model may perform better with preliminary test result inputs specific to the concrete being assessed.

Greater information is required to conclude whether the microstructure of a concrete can be used to predict the carbonation performance. Due to challenges obtaining and quantifying this information it is rarely measured or published alongside carbonation test results, in particular from long term NC tests. This is surprising given the abundance of publications and existing models suggesting that carbonation rate is affected by microstructural properties (Pihlajavaara, 1968; Dhir, Hewlett and Chan, 1989; Basheer, Kropp and Cleland, 2001; Claisse, Cabrera and Hunt, 2001; Valcuende and Parra, 2010; Morandea, Thiéry and Dangla, 2014).

Separating the data into different categories and then analysing the performance of models in these different domains may reveal the success of models to be dependent on other factors which are not explicitly included in their formulation. The analysis may also be improved in future by including yet more data. Difficulties were observed obtaining natural carbonation test results. Due to the slow nature of carbonation, these experiments can take years to effectively carry out, and therefore useable data can be scarce in the literature.

### 3.2.5. Implications for concrete design

A performance-based approach to durability design would define a minimum carbonation resistance for concretes within each durability classification. As a proxy for this, limits are placed by code requirements on  $w/c_{eqv}$  ratio, compressive strength, and cementitious content, making the assumption that controlling these values alone will control a concrete's resistance to carbonation. It is understandable why these values have been chosen to specify the durability classification. They are easily monitored and controlled by the concrete specifier.

The carbonation coefficient directly determines the carbonation depth observed in a concrete exposed to atmospheric CO<sub>2</sub>. Figure 1 suggests that, of the properties specified during design, compressive strength has the strongest relationship to carbonation coefficient. This is reinforced by the superior performance of a strength-based model compared to other model types. However, Figures 2 and 3 suggest that there are subtleties in the  $w/c_{eqv}$  ratio and cement content which are not captured by simply placing limits on these values in design. Difficulties also arise when using the  $w/c_{eqv}$  to compare between OPC and cements containing SCMs, since there is a lack of consensus on the correct k-values for different materials, often depending on the concrete property being investigated or the total volume of SCM being used (Ganesh Babu and Sree Rama Kumar, 2000; Papadakis, 2000; Papadakis, Antiohos and Tsimas, 2002; Papadakis and Tsimas, 2013; British Standards Institution, 2016; Ribeiro, Santos and Gonçalves, 2018). It is demonstrated within the data assessed here that mixes with the same cement content or  $w/c_{eqv}$  ratio can have a wide variety of carbonation coefficients. The result is that the strength-based model in Figure 4 (*fib* model code 2010 model) captures trends more consistently than the stoichiometric or empirical models applied, which both depend on the  $w/c_{eqv}$  ratio (the stoichiometric model also depends on total cement content) to inform their predictions.

## 4. Conclusions

Carbonation is a complex process, for which several possible models exist based on Fickian diffusion behaviour. These models can be categorised as strength based, stoichiometric, microstructural, or empirical.

Of the concrete properties specified by the durability classification process, compressive strength is shown to have the greatest correlation to carbonation performance. In these results, which include many blended cements which are permitted according to the design process of EN 206, the cement content and  $w/c_{eqv}$  ratio do not correlate so strongly with carbonation performance. This implies that, by placing limits on these values, the design process may be artificially and unnecessarily constraining the minimum achievable embodied carbon of concretes specified for carbonation exposure classes.

In this review, a comparison of four different analytical carbonation model predictions against published data from 62 natural carbonation specimens is presented. The concrete mixes analysed cover a broad range of strengths,  $w/b$  ratios, SCMs, and cement contents. The differences between the model performances are assessed statistically. It is shown that, for all the data here compared, the *fib* model code 2010 (*fib*, 2012b) initial estimate model gives the most accurate estimate of carbonation depth, with an R<sup>2</sup> statistic of determination of 0.67, and a RMSRE of 0.35.

Performance based design of carbonation resistant concretes, rather than the current practice of placing limits on mix design parameters, may enable subtleties surrounding  $w/c_{eqv}$  ratio and cement content in mixes to be exploited. There is the potential to prescribe mixes with sufficient resistance to carbonation which fall outside of the limits currently placed by EN 206, and this could also lead to a reduction in embodied carbon due to reduced OPC content. More research is required to fully explore this potential.

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