Statistical analysis of the carbonation rate of concrete

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ABSTRACT

The carbonation rate of concrete has implications for the lifecycle carbon emissions of concrete. This paper describes the reported effect of several variables on the rate of concrete carbonation and collates a data set of measurements published in the literature. Many studies producing predictive models for the carbonation rate constant, K, use only small data sets. 1999 measurements of carbonation depth as a function of time and other variables were collected for analysis. Models in the form $\ln(K) = a + bI1 + cI2 + \ldots$ have been produced by which the rate of carbonation can be predicted. Hierarchical Models were used to combine different authors' data and introduces a new explanatory variable called 'origin', which indicates whether the concrete was taken from a working structure or cast specifically for experiments. Two models of the carbonation rate using concrete properties have been produced, allowing prediction of K over a range of conditions and compositions.

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1. Introduction

Concrete is used in vast quantities and its use has given architects and engineers the ability to design and construct buildings and infrastructure that have greater functionality than would otherwise be possible. However, it does degrade over time; one process which can contribute to this is the absorption of carbon dioxide, known as carbonation. The aim of this work is to develop, using statistically robust procedures combined with a very comprehensive literature review, correlations to predict rates of carbonation of cementitious materials, based on their methods of production and use.

Carbonation is the reaction between the calcium-based phases in concrete and carbon dioxide from the air, which enters the concrete via the pore network. Many studies have attempted to measure the rate of carbonation in concrete. However, for legitimate reasons the studies generally tend to concentrate on measuring the carbonation rate or depth in a limited range of concretes and environments. Indeed, in many studies the type and properties of the concrete is unknown. However, by bringing these numerous papers together for analysis, an attempt to draw overall conclusions about the nature of concrete carbonation, and better estimations of the rate of carbonation, can be made for a variety of cement types and conditions.

The paper starts with a description of how carbonation proceeds and discusses some of the variables that affect its rate. The state of data in the literature is then described and the distribution of the carbonation rate constant, K, is discussed. Next, hierarchical models for the

carbonation rate constant are presented and discussed. Finally, conclusions are drawn.

1.1. Mechanisms of carbonation

Concrete carbonation occurs between hydrated calcium compounds (which originate from the reaction between water and cement) and carbon dioxide when they are both dissolved in water held in the pore network of concrete. This network allows the transport of gases and, to a lesser extent, liquids within the concrete [1]. The calcium carbonate product then leaves solution and is precipitated. Simple models relating to the diffusion of gases within the pore network, dissolution of CO_2 and calcium hydroxide (CH) into the pore water and their subsequent reaction tend to produce models which imply that there is a reaction front; that is, at any time past the initiation of carbonation there is a zone between the exposed surface of the material and the carbonation front which is fully carbonated and one beyond the front which is completely uncarbonated. The rate of CH dissolution is dependent on the difference between the equilibrium and actual concentrations of OH^-, and the overall carbonation rate is dependent on the relative humidity in the concrete, which determines whether the rate-determining step is gaseous diffusion of CO_2 into the pore network or dissolution from the gas to the pore water within the network [2]. CH has a low solubility in water but due to the slow rate of CO_2 diffusion this does not seem to be a rate-determining step [3]. Calcium silicate hydrate (CSH) does not necessarily carbonate at the same rate as CH and thus the simple models are quite simplistic [4]. Yet more complexity is added by the fact that the carbonation product ($CaCO_3$) is larger than the original

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CH and CSH [4], so carbonation may in fact partially or completely block pores through which CO_2 diffuses.

The difference in properties and reaction rates of CH and CSH has led to the suggestion that there are separate carbonation fronts for CH and CSH [4,5]. However, studies undertaken with techniques such as thermogravimetric analysis (TGA) have shown that the reaction front is actually a zone of finite width which can span several millimetres with concentration gradients of relevant phases [5–9]. This is, however, disputed by some [10,11]. For the sake of reporting and practicality, however, many researchers measure carbonation as a sharp reaction front using a solution of phenolphthalein indicator in water or ethanol. Phenolphthalein is red/pink at pH > 9 (uncarbonated concrete) and colourless at pH < 9 (carbonated concrete). This transition point is then reported as the 'carbonation depth'. Despite its simplicity, this method is not as accurate as TGA [5,7,12–16].

1.2. Approximation of carbonation depth

The carbonation depth is defined as the distance between the exposed surface of the sample through which the CO_2 enters and the carbonation front. The depth of carbonation as a function of time can be approximated by using four main assumptions which lead to Eqs. (1) & (2):

- All gases within and without the cementitious material are ideal gases;
- The reaction of CO_2 with the material is instantaneous (i.e. diffusion of CO_2 is the rate-determining step);
- Diffusion is one-dimensional and conforms to Fick's first law of diffusion;
- The initial concentration of species which can carbonate in the concrete does not vary in space.

$$x = \sqrt{\frac{2Dp_{ext}t}{RTQ}} = K\sqrt{t} \qquad (1)$$

$$K = \sqrt{\frac{2Dp_{ext}}{RTQ}} = \sqrt{\frac{2D\varphi_{CO_2}}{Q}} \qquad (2)$$

here, D is the diffusion coefficient of CO_2 in the concrete ($m^2.s^{-1}$), φ_{CO2} is the concentration of CO_2 in the concrete ($mol.m^{-3}$), x is the depth of the carbonation front in the concrete, R is the universal gas constant ($8.314\ J.K^{-1}.mol^{-1}$), T is the absolute temperature of the system (K), p_{ext} is the partial pressure of CO_2 in the bulk gas outside of the concrete, Q is the molar concentration of material able to be carbonated in the concrete ($mol.m^{-3}$) and K is the carbonation rate constant ($m.yr^{-0.5}$). This is a common method of approximation [2,4,5,7,10,13,18–27]. In certain exceptional cases the rate of carbonation seems to follow $t^{0.4}$ [25,28] but the vast majority of work suggests that the dependency is on $t^{0.5}$. K has been shown in many studies to depend on many other variables, as discussed below [7,20,29–34]. Note that most studies quote the carbonation rate constant in $mm.yr^{-0.5}$.

1.3. Variables affecting the rate of carbonation (carbonation rate constant) in cement

One can classify variables affecting the carbonation rate constant K into two main groups [22]:

- variables that arise from the environment in which the cement was mixed, cured and stored;
- variables that arise from the difference in composition and casting between different mixes of cement and concrete. This includes type of cement, aggregate and sand as well as additives and substitutes and the overall density and mix ratio.

These are discussed in turn below.

1.3.1. Environmental variables

- Relative humidity. At high humidity more of the pores will be completely filled with water, rather than lined with an aqueous film. The complete filling of pores with liquid water reduces the diffusivity of the gases because they move through air 10^4 times faster than through water [35]. Some humidity is required, however, to ensure that the aqueous film is thick enough so that there is ample volume for the aqueous carbonation reaction to happen. Carbonation happens fastest at a relative humidity of 50–70% [19].
- Exposure to weather. Most studies e.g. [8,18,34,36,37] have shown that samples kept inside carbonate more quickly that samples left outside, and samples placed outside but sheltered from the elements carbonate much more quickly than samples exposed to rain. Galan et al. [23] proposed that this is due to rain filling the pores of exposed concrete (waterlogging), hindering the diffusion of CO_2. The effect of exposure to weather is very variable both between studies and within studies. Some studies show the ratio of $K_{sheltered}:K_{exposed}$ to be between 1 and 2 whilst others show ratios of greater than 8 [8,34,37,38]. One study by Matthews [39] shows a range of ratio from 0.5 to 26 for identical samples left sheltered and exposed. This suggests that some of the processes involved in carbonation within the concrete are not well understood; the use of inadequate measurement techniques (such as phenolphthalein solution) may also contribute to this effect.
- Plastering. Roy et al. [19] reported that a 30 mm thick plaster layer prevented any carbonation in a 19-year-old structure in Singapore in which unplastered concrete had a carbonation rate constant, K, of $5.05\ mm.yr^{-0.5}$. Huang et al. [13] found that a 50 mm thick plaster layer prevented any carbonation in a 35-year-old structure in which unplastered concrete had a carbonation rate constant of $1.38\ mm.yr^{-0.5}$. Heuristic estimates seem to assume a much lower effect of plaster on K. Lagerblad [4] estimated the decrease in the carbonation rate constant for cement with plaster to be approximately 20% whilst Gajda [6] estimated the decrease in rate to be approximately 50%; however, neither author provided any evidence for their respective values.
- Curing. Ali & Dunster [34] concluded that the quality of curing has no large effect on the rate of carbonation of ordinary Portland cement (OPC, also known as CEM I [40]), concrete but in samples made with pulverised fly ash (PFA) cement (a.k.a. CEM II) or ground granulated blast furnace slag (GGBS) cement (a.k.a. CEM III) the effect was greater. The type of formwork applied during the curing process had a significant effect on carbonation rate, but the sample size for each of the formworks was low and so no definitive conclusions could be made. Other researchers have found that water-curing greatly decreases the subsequent carbonation rate of concrete compared with air-curing, and that a longer water-curing period leads to a slower rate of carbonation, although water-cured concrete tends to catch up with air-cured concrete over time [41–43].
- Cracks within concrete can lead to increased carbonation and maximum carbonation depth due to lower diffusion resistance in the crack compared with the bulk material. The size of the crack is of importance, and Liang et al. [44] developed a modified empirical carbonated crack depth approximation.

1.3.2. Compositional variables

- Water to cement (W/C) ratio. The amount of water in concrete during casting affects not only the humidity within the material but also the