Cement & Concrete Composites 52 (2014) 42–53

Contents lists available at ScienceDirect

Cement & Concrete Composites

journal homepage: www.elsevier.com/locate/cemconcomp

Reactive transport modelling of long-term carbonation

O.P. Kari *, J. Puttonen, E. Skantz

Aalto University, School of Engineering, Department of Civil and Structural Engineering, PO Box 12100, FI-00076 Aalto, Finland

ARTICLE INFO

Article history:
Received 26 October 2013
Received in revised form 24 February 2014
Accepted 10 May 2014
Available online 21 May 2014

Keywords:
Carbonation
Concrete
Model

ABSTRACT

Concrete specimens of sulphate resistant Portland cement (SRPC) exposed to natural carbonation in a controlled environment for 13 years revealed that the carbonation was significantly underestimated by accelerated tests and extrapolation by a linear diffusion equation. The results confirmed that carbonation as a phenomenon is too complex to be predicted by a conventional diffusion equation for periods considerably exceeding the experimentally covered period. A comprehensive approach consisting of a thermodynamic model and a statistical methodology to simulate long-term carbonation verified by versatile experimental data was presented. As an application of the method, long-term carbonation was simulated for the SRPC concretes.

1. Introduction

Reinforcing steel embedded in concrete is protected from corrosion through the alkalinity of the surrounding concrete. Several environmental factors can break down the passive state of steel leading to possible initiation of reinforcement corrosion. Concrete carbonation is known to be the major phenomenon that can decrease the pH-value of concrete, exposing reinforcement to corrosion.

The aerial carbonation process can be summarised by the following reaction mechanism [1]:

$$CO_2(g \rightarrow aq) + Ca(OH)_2(s \rightarrow aq) \rightarrow CaCO_3(aq \rightarrow s) + H_2O \qquad (1)$$

where the atmospheric carbon dioxide diffuses into the unsaturated concrete and dissolves into the pore solution mainly as HCO_3^- and CO_3^{2-}. They react with calcium hydroxide that has been also dissolved into the pore water, to form calcium carbonate, as well as other CO_2-based cement hydrates. Free water and calcium carbonate, which quickly forms a solid matrix, are the main products of the reaction. The amount of solid $Ca(OH)_2$ helps to maintain a high pH as long as there is $Ca(OH)_2$ available for reaction [2]. The stabilities of calcium silicate hydrate (C—S—H), AFm and AFt phases are also dependent on the high pH and Ca ions in the pore solution. After consumption of $Ca(OH)_2$, C—S—H first decalcifies and then decomposes decreasing further pH-value and the concentration of Ca ion. This leads to decomposition of the other main phases into new compounds and alteration of concrete [3]. Carbonation rate and carbon dioxide diffusion are generally dependent on relative humidity, temperature, external CO_2 concentration, and concrete material characteristics, such as the cement type.

A simple and widely used method for determining the depth of carbonation is to use a phenolphthalein indicator, which will turn purple in the zones of higher pH-values. The indicative threshold pH-value can have, however, a relatively wide range [4,5]. The front of a phenolphthalein indicator does not depend on the exact degree of carbonation [6]. As a function of the distance from the surface, the degree of carbonation (0–100%) can alternatively be determined by measuring pH-values directly from the concrete pore solution. Compared to the phenolphthalein method, a more reliable approach to determine the concrete carbonation is to combine the measured pH-value distribution to the amounts of the cement hydrates $Ca(OH)_2$ and $CaCO_3$ that are the main components of carbonation reactions. Nevertheless, the relation between the pH-value and the carbonation degree may significantly vary from case to case [6,7]. The pH-value can vary with the carbon dioxide concentration of the surrounding atmosphere [8].

Typically, an accelerated carbonation test performed under high CO_2-content (1–50%) is used for the prediction of the long-term carbonation of concrete by applying [9]. The results of the accelerated tests, which have been measured with phenolphthalein are then conventionally analysed by fitting them to an empirical linear diffusion model [10,11]. This approach disregards the effect of time-dependent changes on the material properties of concrete or on environmental conditions, such as temperature, relative humidity, and CO_2-content, which are relevant for the case-specific carbonation [12]. It may also be doubted, whether the conventional methods are able to describe the carbonation accurately enough, as the interaction of the various complex phenomena is disregarded.

* Corresponding author. Tel.: +358 9 47001.
E-mail address: olli-pekka.kari@aalto.fi (O.P. Kari).

http://dx.doi.org/10.1016/j.cemconcomp.2014.05.003
0958-9465/

Precipitation and dissolution of minerals as well as the pH-value during the exposure greatly depend on the binder used. Typically, a sulphate resistant Portland cement (SRPC) is used as a binder in concretes subjected to chemically aggressive environments. However, the authors did not succeed in finding any studies about long-term carbonation of SRPC concretes. The observed lack of information of the carbonation of SRPC concretes combined with their importance for industrial buildings were the reasons for using SRPC concretes in this study, as the deterioration mechanisms of SRPC concretes may differ from those made of ordinary Portland cements (OPC).

The applicability of methods based on linear diffusion equations and accelerated tests for estimating the long-term carbonation were evaluated using the results received for natural carbonation during 13 years in controlled circumstances. The environmental conditions were constant, that is, the evaluation of the behaviour of the concretes and the testing of the modelling approach were carried out without any fluctuations caused, for example, by wetting and drying cycles. The developed approach to the prediction of carbonation rest on thermodynamical analysis and case-specific parameters, which are introduced in the study. The verification of this approach was made by utilising long-term experimental data created in this research. As accuracy and uncertainty are always connected to measured data, the study also presents a procedure to quantify the effect of uncertainties on the simulated progress of carbonation process.

2. Prediction of carbonation by accelerated test and Fick's diffusion law

2.1. The models for estimating carbonation depth based on Fick's diffusion law

The classical method for estimating carbonation as a function of time is to fit the results of the carbonation depths measured by phenolphthalein to the empirical model, which obeys a basic square root assumption of carbonation as

$$x = k \cdot \sqrt{t} \tag{2}$$

where x is the depth of carbonation (mm), t the exposure time (years), and k is the empirical coefficient which describes the speed of carbonation (mm/$\sqrt{}$year). A common feature for the conventional models presented in the literature [11,13,14] is that they can be reduced to Eq. (2), where the coefficient k sums up the influence of various factors [15]. Therefore, the k value is usually determined through the relationship between the CO_2 concentration (%) in the accelerated a and natural environment n as

$$\frac{k_a}{k_n} = \sqrt{\frac{[CO_2]_a}{[CO_2]_n}} \tag{3}$$

2.2. Experimental assessment of conventional models

2.2.1. Used specimens and environmental conditions

SRPC concrete specimens were cast for the accelerated and long-term natural carbonation tests in 1997 [16]. These beam-shaped specimens had dimensions of $90 \times 90 \times 500$ mm^3. After the removal of the formwork at the age of 1 day, the specimens were kept in water for 28 days. In the next phase, the specimens were exposed to accelerated carbonation tests and were stored in the carbonation chamber with environmental conditions of RH 70 ± 5%, temperature 20 ± 2 °C, and CO_2 content 4 ± 0.5%. The carbonation depth was measured with phenolphthalein solution from each surface of the concrete pieces. The pieces with a width of 20 mm were cut from the end of the specimens at prescribed points of time. Since the age of 28 days, the specimens used for determining the long-term natural carbonation under controlled environment were stored in average conditions of RH 70 ± 5%, temperature 12 ± 2 °C for the first 75 months and then 81 months in conditions of RH 35 ± 5%, temperature 22 ± 2 °C. The average CO_2 content was 0.038%. In total, the exposure time was 13 years for the samples used in the study. The environmental conditions were changed in the middle phase to simulate the environmental changes of industrial applications in mind. The compositions of the concrete mixes SR04 (w/c 0.43) and SR05 (w/c 0.50) are presented in Table 1, where is also given the composition of cement used for their casting. According to the petrographic analyses performed [16] for the aggregates, potentially alkali-reactive aggregates, or excessive amounts of micas, sulphates or clay minerals were not observed. Feldspar (57%) and quartz (29%) were the main mineral constituents of fine aggregates, whereas the main rock constituents in aggregates were granite and diorite/amphibolite with their relative proportions of 65% and 15% of coarse aggregates, respectively.

2.2.2. Comparison between the natural carbonation and the prediction given by accelerated tests and conventional methods

The depth of carbonation was regularly determined for both concretes by phenolphthalein during the 70 months of the accelerated carbonation tests. The duration of the accelerated test can be considered remarkable long. Fig. 1 represents the results of the accelerated tests and the best fits of Eq. (2) to the data points leading to values of 1.84 and 2.18 mm/$\sqrt{}$month for the parameter k in Eq. (2) (exposure time t defined as months) for the concretes SR04 and SR05, respectively. The speed of carbonation in accelerated test k_a is approximately tenfold to the coefficient of natural carbonation k_n according to Eq. (3). As a result the natural carbonation should be 2.3 and 2.7 mm after 13 years based on the reduced k values in Eq. (2). The carbonation depths measured by phenolphthalein for the concrete mixes SR04 and SR05 held 13 years under natural conditions were 3.0 mm and 7.5 mm, respectively. The results reveal that the carbonation depths based on the prediction given by accelerated test deviate clearly from the values of natural carbonation, especially in case SR05. Generally, the carbonation proceeded much faster than expected by the accelerated tests.

In the accelerated tests the progress of concrete carbonation did not obey Eq. (2), especially in the early stages of testing. Neither can the observed intersection of the measured values of the carbonation depths of the concrete mixes be predicted by Eq. (2). The length of the accelerated test was remarkably long compared to commonly used test periods, which should increase the validity of the method despite the experimental campaign with changing environmental conditions. The natural conditions were not as stressful from the carbonation viewpoint as the accelerated tests, where the surrounding temperature was 20 ± 2 °C, whereas the temperature in the natural conditions was 12 ± 2 °C for 75 months. During the last 81 months the temperature was 22 ± 2 °C in the natural conditions but the relative humidity was only 35% compared to the 70% in the accelerated test.

The conclusion was that the long-term carbonation cannot be estimated reliably by combining a conventional linear diffusion method and the results of accelerated carbonation tests. The carbonation as a phenomenon was confirmed to be more complicated than conventional diffusion models assume. It is obvious that in the simulation, it is also necessary to model altering physical and chemical phenomena.