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A note on limitations of the use of accelerated concrete-carbonation tests for service-life predictions

A. Muntean, S. A. Meier, M. A. Peter,
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A note on limitations of the use of accelerated concrete-carbonation tests for service-life predictions

Adrian Muntean* Sebastian A. Meier* Malte A. Peter*
Michael Böhm* Jörg Kropp†

Abstract

Concrete carbonation is a process that can limit the lifetime of reinforced concrete structures. The resistance of concrete samples to carbonation is usually determined by accelerated tests under relatively high CO_2-concentrations and a fixed relative humidity. No general agreement exists on *whether* and *how* the results of these experiments can be extrapolated to a natural setting. This note presents a partial review of existing extrapolation strategies, particularly of explicit prediction formulas. A summary of the problems and limitations which are known from experiments and theoretical modelling is given. Special focus is directed to the different moisture transport characteristics in both natural and accelerated settings. Some strategies are proposed on how to deal with the problems.

Key words and phrases: Concrete carbonation, accelerated test, natural exposure, moisture, mathematical modelling, service-life prediction, extrapolation procedures and their limitations

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1 Introduction

A common problem with reinforced concrete structures is the deterioration brought in by the corrosion of reinforcing steel and the subsequent spalling of concrete. This is most often caused by moisture and aggressive species (like Cl^-, SO_4^{2-} etc.) advancing to the location of the steel reinforcements where it causes the corrosion. This process is often aggravated by carbonation, which is the result of the action of environmental conditions bringing about a drop in the alkalinity of the concrete over many years.

In order to measure a significant carbonation penetration in concrete-based materials in a short time interval, accelerated test methods have been proposed. Compare [Par90, CSK91], e.g., for an assessment of various methods of measuring the depth of carbonation. The need to determine the depth of carbonation requires a deep understanding of the limitations of the tests used to detect carbonation and of the meaning of the test results. Relying on such information, strategies capable of extrapolating the results of accelerated tests to outdoor carbonation conditions have to be proposed. Unfortunately, no general agreement exists on *whether* and *how* the results of these experiments can be extrapolated to a natural setting.

The scope of the present work is to give a *partial review of existing extrapolation strategies* (namely of complex models and explicit prediction formulas) as well as some of their drawbacks. It aims to complete other reviews already existing in the literature (compare sections 4.1 and 3.1).

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*Centre for Industrial Mathematics, FB 3, University of Bremen, Postfach 330 440, 28334 Bremen
†University of Applied Sciences, FB 3 Civil Engineering (BAU), Neustadtswall 30, 28199 Bremen

The note is organised as follows: A brief motivation and description of the accelerated tests and their setup is presented in section 2. Several theoretical and semi-empirical models are concisely mentioned in section 3. Section 4 contains a summary of problems and limitations which are observed in experiments and are underlined by theoretical modelling. Special attention is paid to the different moisture transport characteristics in both natural and accelerated settings. A few strategies how to deal with the problems are proposed in section 5. We conclude this review by a short summary (section 6).

2 Accelerated carbonation tests

2.1 Why accelerated tests?

It is nearly impossible to reproduce natural exposure conditions by means of a simple test method. However, once the accelerated tests are performed, their results can offer useful information for real-time prediction provided that the limitations of the testing conditions are known. Unfortunately it is very often not clear how this information should be interpreted (extrapolated). Besides this predictive feature, the accelerated tests represent a way to investigate a series of extreme carbonation-related behaviours (e.g., carbonation does not take place, carbonation is extremely fast, a clogging situation occurs, etc.). On the other hand, it constitutes an appropriate framework (a comparative tool) to compare the quality of several types and treatments of concretes (curing time, water-to-cement ratio, etc.) in what the carbonation penetration is concerned.

2.2 Some test details

Detailed description of accelerated tests are given, for instance, in the EU standard[1] [Eur98], but also in [Kro83, Bie88, Bun94, Sis04, CSK91], and some of the references therein[2]. A phenolphthalein colour test can be used to estimate the depth of carbonation by testing the pH of concrete (carbonation reduces pH). Upon application of the phenolphthalein solution to a freshly fractured or freshly cut surface of concrete, noncarbonated areas turn red or purple while carbonated areas remain colourless. Sampling can allow the average and standard deviation of the carbonation depth to be calculated. If the carbonation depth is compared with the average width of reinforcement cover, then the amount of potentially depassivated steel can be estimated.

In some aggregates, accurate phenolphthalein readings are difficult to obtain. Some concrete mixes are dark in colour and a colour change may not be visible. Care must be taken that no contamination of the surface occurs from dust and the phenolphthalein sprayed surface must be freshly exposed or it may be carbonated before testing. It is also possible for the phenolphthalein to bleach at very high pH, e.g. after electrochemical chloride extraction or realkalisation. If the sample is left for a few hours, it will turn pink. There can also be problems on buried structures where carbonation by ground water does not always produce the clear carbonation front induced by atmospheric carbon dioxide ingress.

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[1] Observe that this standard explains *how* an accelerated test should be done, but it does neither say *how* nor *whether* one should extrapolate the test results to natural conditions.

[2] In case of an accelerated carbonation test, it is worth noting that the humidity, temperature, and the CO_2 concentration level in the carbonation chamber are monitorised. *Accelerated* basically means that the CO_2 concentration in the chamber is essentially higher than in a normal atmospheric situation. Note that usually constant conditions are imposed. In most of the situations, two main *assumptions* are taken into consideration: (1) The relative humidity of the sample equals that of the carbonation chamber; (2) The hydration reactions are complete (or *almost* complete).

3 Extrapolation methods

Cf. [SAC03], no general agreement exists on *how* to extrapolate the penetration depths measured in an accelerated test to a natural setting. There are various models in the literature which can be roughly split in two conceptually different categories: The *explicit laws* for the penetration depth have a longer history. They are based on either empirical or theoretical considerations, or on a mixture of both. In contrast, there are *complex models* that usually consist of systems of partial differential equations modelling the full carbonation process. Explicit solutions for these models exist only in very special cases, therefore in general they have to be solved numerically.

3.1 Explicit prediction formulas

In practice, those models are preferred which are easy to handle. Usually they consist of *one explicit formula* predicting the carbonation depth at a given time t. They are sometimes called *carbonation laws*. However, they can only hold under several strong assumptions and it is not at all obvious how certain parameters like the cement type or the water-to-cement ratio enter into the coefficients.

The most often used carbonation law is the so-called *standard-$\sqrt{t}$-law*. Based on Fick's first law of diffusion, the carbonation depth at time t, which we denote by $s(t)$, is given by

$$s(t) = \sqrt{\frac{2D_{\mathrm{CO}_2}[\mathrm{CO}_2]t}{[\mathrm{Ca(OH)}_2]}}, \qquad \text{for all } t > 0. \tag{1}$$

In (1), the coefficient D_{CO_2} represents the effective diffusivity of gaseous CO_2 whereas $[\mathrm{Ca(OH)}_2]$ is the initial amount of $\mathrm{Ca(OH)}_2$ that can react with CO_2.[3] The above law can be derived as a *pseudo-steady-state solution* of a reaction-diffusion model if an instantaneous reaction of CO_2 with the $\mathrm{Ca(OH)}_2$ available by dissolution is assumed. See [Kro95, Sis04], e.g., for such a derivation. Absorption delays for CO_2, moisture effects, and transport of other species than gaseous CO_2 are neglected.

A generalisation of (1) is given by Papadakis et al. [PVF89]. In their study, they include a late stage of hydration reactions as well as additional carbonation reactions of CSH, $\mathrm{C_2S}$, and $\mathrm{C_3S}$ and they give explicit conditions for the pseudo-steady-state approximation (PSSA) to be valid. Their approach leads to the following expression to estimate the penetration depth

$$s(t) = \sqrt{\frac{2D_{\mathrm{CO}_2}[\mathrm{CO}_2]t}{[\mathrm{Ca(OH)}_2] + 3[\mathrm{CSH}] + 3[\mathrm{C_2S}] + 3[\mathrm{C_3S}]}}, \qquad \text{for all } t > 0. \tag{2}$$

Some authors have proposed modifications of the $\sqrt{t}$-law (1) due to empirical or theoretical considerations. Sisomphon [Sis04, Sis05] observes a better fitting to his measured penetration depths with an exponent of $n = 0.4$. Therefore, the law

$$s(t) = \sqrt{\frac{2D_{\mathrm{CO}_2}[\mathrm{CO}_2]}{[\mathrm{Ca(OH)}_2]}}\, t^{0.4}, \qquad \text{for all } t > 0, \tag{3}$$

is used for prediction. The deviation from (1) is explained by the pore reduction due to carbonation. See section 4.2.1. Using atmospheric conditions of 3% CO_2 in the acceleration chamber, an acceleration of the penetration by roughly a factor of 10 is obtained. In contrast, Parrott [Par92] relates the exponent n empirically to the relative humidity in the chamber, i.e. $n = f(\mathrm{RH})$.

Note that the seemingly small changes in the exponent cause a dramatic change in the prediction. Using the *equivalent testing time* notion[4] we denote by t^{real} the time needed to carbonate

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[3] To be more precise, the quantity [A] in (1)–(3) denotes the initial concentration of species A. This is assumed to be completely available to the carbonation reaction.

[4] This was introduced by Ho and Lewis, e.g. See [SAC03, HL87].

1 cm of a concrete specimen under natural conditions (0.03% CO_2), and by t^{acc} the respective time in an accelerated chamber with 3% CO_2. Then by (3) we obtain

$$t^{\mathrm{real}} = 316\ t^{\mathrm{acc}}. \tag{4}$$

On the other hand, using (1) or (2) we obtain

$$t^{\mathrm{real}} = 100\ t^{\mathrm{acc}}. \tag{5}$$

The obvious question arises: *Which prediction is the appropriate one?*

Two other theoretical models should also be mentioned: The model by Bakker [Bak64] is also based on a steady-state assumption and includes *drying phases* during which no carbonation can occur. See also section 4.2. The model by Tuutti [Tuu82] is a non-steady-state approximation based on moving boundaries. Further approaches have been developed by Hilsdorf et al. [MC99] and Schießl [Sch76]. Besides the semi-empirical and asymptotic approaches, some semi-analytic techniques have also been employed to predict the penetration depths. See [LL03], e.g. Due to the complexity of the full carbonation problem, their success is somehow limited. For still more models we refer to the overviews in [Kro95, SAC03, Cha99, Bun94], e.g. See also the list of carbonation laws in [Sis04], table 2.2, p. 30.

It should be noted that there are not only a variety of models, but also various possible ways how to use them. For example, the standard-$\sqrt{t}$-law can be used for prediction without any testing method if the values of $[\mathrm{Ca(OH)_2}]$ and $D_{\mathrm{CO_2}}$ are known. Since particularly the latter parameter is usually difficult to measure, it is nevertheless common to assume the structure $s(t) = k\sqrt{[\mathrm{CO_2}]t}$ and to fit the parameter k to the measurements in the accelerated test.

3.2 Complex models

In the last decades, large models have been developed in order to simulate the carbonation process numerically. The general approach is to collect mass balances (and possibly momentum and heat balances) of the active species. This procedure yields coupled systems of conservation laws (usually, ordinary and partial differential equations). We call them generically *isoline models.* For more details on isoline approaches of the carbonation problem, see the contributions by Roelfstra et al. [HRW83], Saetta et al. [SSV93], Papadakis et al. [PVF89], Maekawa et al. [MIK03], Bary and Sellier [BS04], etc. See also [MPMB05, PMMB05]. Numerical simulations in 2D have been done by Saetta et al. [SSV95, SV04], Steffens [Ste00], Burkan Isgor [Isg01], and Schmidt et al. [SMB05]. As far as we are aware of, simulations of concrete carbonation in 3D have not been done yet.

Since in both settings (accelerated and natural) the reaction part dominates the transport, in most cases a relatively thin reaction zone is initially formed which separates the carbonated region from the uncarbonated region and travels into the material. The observation of this pattern formation (an internal more or less sharp *reaction layer*) motivates the introduction of conceptually different models to describe the dynamics of this internal layer. We refer to them shortly as *moving-boundary models* or *moving-interface models.* Such models have been proposed for carbonation by Tuutti [Tuu82], Brieger and Wittmann [BW86], and by Böhm et al. [BKM03b, BKM03a] and Muntean [Mun05]. For more details on the latter approach, see also [MB04b, GM03, MB04a].

Most of the models are based on macroscale formulations. Such macromodels usually arise from exact micromodels by averaging techniques like periodic homogenisation (see [CD99], e.g.) or the volume averaging method by Whitaker [Whi99]. See particularly [SMB99, SMSB05] for an application of the latter method to concrete-based materials. By the first method, a variety of mixed *micro-macro models* can also arise where microstructure effects are described by a local cell problem. See [Mei04, Pet03] for applications to the concrete carbonation problem. Such models can capture effects on numerous spatial scales such as different pore sizes in cement-based materials or fractures.

The effective usage of a complex model combining measured data from accelerated tests for prediction purposes is nontrivial. Particularly, it leads to *parameter identification problems.* See, e.g., [BK89] and references therein for a general overview. This subject has not been treated in detail for the carbonation problem, at least to our knowledge.

4 Problems and limitations

4.1 Comparisons in the literature

Unfortunately there are very few experimental works, in which the authors directly compare results of accelerated tests with those under natural conditions. We are not aware of extensive studies where several different external CO_2-concentrations and several RH levels are imposed on samples having identical chemical composition and also same mixing/curing/drying (hydration degree) treatment. However, there are many hints in the experimental work indicating that accelerated carbonation tests cannot be extrapolated to a natural-exposure scenario by a simple scaling only related to the ratio of the CO_2-concentrations.

Andrade et al. [SAC03] compare the carbonation of a set of concrete samples under natural and accelerated (5% and 100% CO_2) testing conditions. Roughly, they obtain a propagation of the carbonation depth which is 5 and 40 times faster, respectively, than in the natural case. A comparison with the theoretical models by Tuutti [Tuu82] and Bakker [Bak64] and with the empirical model by Parrott [Par94] shows that the models are in the right range but overestimate the carbonation penetration. Additionally, some contradictory trends are illustrated when different types of additions are used. It is emphasised that predictions should only be made between the same types of concretes. Moreover, they conclude that experimental results with $4 - 5\%$ CO_2 cannot be simply extrapolated to larger values of CO_2. Similar effects have been observed by Ishida et al. [IMS04] by means of numerical simulations. The authors investigate the behaviour of their model under different CO_2 concentrations and also with different additions in the concrete. They conclude that accelerated and natural tests are not always analogous.

Note that even in those references, where a simple scaling between the two tests is assumed, there is no agreement about the choice of the factors by which carbonation advancement is increased or decreased. See [Ver58, HL87], e.g. Papadakis et al. [PVF89] also compare the case of experimental data where different atmospheric CO_2-concentrations are successively imposed in the carbonation chamber. In their case, the measurements seem to be in excellent agreement with the law (2) for the carbonation penetration proposed in the same paper. On the other hand, Chaussadent [Cha97] reports experimental results where a high CO_2 content in the atmosphere even leads to a slower carbonation rate.

4.2 Possible causes of discrepancies

There are several physico-chemical processes, exposure conditions, and parameters, which can show a different behaviour under accelerated compared to natural conditions. There are two significant (technical) differences that appear in the setup of accelerated tests: (1) The type of exposure conditions (higher CO_2 level than it is expected in the atmospheric conditions, constant relative humidity, fixed temperature, etc.), and (2) the shorter duration of the whole process. The first fact is somehow more obvious, whereas the latter one can produce some hidden effects. In the following subsections, we try to review the most important discrepancies between the two test methods. They are all somehow well-known by the community dealing with this subject. However, a lot of effects are concurring and the precise interplay is *not* known such that even general trends are extensively discussed and *differently interpreted* in the literature. Note also that there may still be further effects that are not considered here.

4.2.1 Changes in the microstructure due to carbonation

Besides the decrease in pH, another important consequence of the carbonation process is the change induced in the microstructure. A detailed description of this phenomenon can be found, for instance, in [BKH87, NP97, CBBH$^+$00, Bie88]. In particular, at least in the case of ordinary-Portland-cement-based materials (OPC), the fast precipitation of the $CaCO_3$ produced by carbonation can lead step by step to a clogging of the pores. This locally hinders any further transport of CO_2. Macroscopically, the clogging of the pores can be numerically captured by including a porosity variable in the models which can vary in time or even in space. See existing porosity models in [PVF89, SON90, MIK03] (linear relationships), [MPMB05] (exponential decay), [BS04, Ort94] (dynamical models), e.g. Alternatively, a time-dependent effective transport coefficient for gaseous CO_2 can be used. It is assumed [Sis04] that due to a decrease in porosity a standard $\sqrt{t}$-law will overestimate the carbonation for large times.

In [CSH05], the authors observe experimentally that in the accelerated test a prolific development of calcite crystals takes place in the pores and fissures through which the carbonic anhydride flows. On the other hand, under natural conditions carbonation is much slower and similar levels of crystals development are not reached (at least not within 6 months).

4.2.2 Effects of other reactions

There are several chemical reactions inside the concrete competing with the carbonation of $Ca(OH)_2$. By *competing* it is meant that partially the same reactants are involved, for instance CO_2 or CSH, e.g., to deplete $Ca(OH)_2$. They also have an implicit impact on the carbonation process by altering the microstructure and consequently the transport properties.

- *Competition between* CSH *and* $Ca(OH)_2$ *carbonation*

  In case of samples with OPC (in both acc. and nat. testing conditions), a competition between the carbonation of CSH phases and that of $Ca(OH)_2$ always exists. It is however not always clear whether this competition is strong, or whether the CSH phases are really accessible to CO_2 or not. If they are, then their carbonation has to be investigated in parallel to the bulk carbonation. See [PVF89, PMMB05, Ste00], e.g.

- *Competition of a late stage of hydration, with the carbonation of* CSH *phases and* $Ca(OH)_2$

  In accelerated tests, one usually assumes the hydration to be complete. If this limitation is not satisfied (as it is usually the case for natural carbonation), then an additional competion of C_2S and C_3S with CSH and $Ca(OH)_2$ may occur. See [PVF91, PVF89, PMMB05, Par85].

- *Effect of nonreacting additions on* $Ca(OH)_2$ *carbonation*

  In some cases, mineral additions like

  (a) blast furnace slag,
  (b) pozzolanic additions (fly ash, silica fume, e.g.),
  (c) or something else (biologic materials, e.g.)

  are added in order to obtain samples with improved mechanical properties. In concrete-based materials containg (a), the carbonation process is simply faster than in OPC materials. This follows the rule *more slag, less* $Ca(OH)_2$. We concisely discuss the case (b) in the next item. We do not address our attention to case (c).

- *Competition of a late stage of hydration and pozzolanic reactions with the carbonation of* CSH *phases and of* $Ca(OH)_2$

  Although the complex chemistry of such scenarios is quite well understood, the interplay between hydration, pozzolanic, and carbonation reactions with the underlying transport mechanisms (especially for case (b) above) is not completely understood. It may finally result in a fast carbonation. Furthermore, it is not obvious how the concrete porosity evolves in such cases. The evolution of the porosity (in time and space variables) seems to be determined by the complex competition between several reactions depleting $Ca(OH)_2$, and the difference in the molar volumes of $Ca(OH)_2$ and calcite-based products. See, e.g., [Sis04, FS04] for experimental data and modelling, [PVF89, PVF92, PVF91] and [Bie88, Tay97, KS87] for more on chemistry.

- *Related competition scenarios*

  Other alkaline species than $Ca(OH)_2$ may produce calcium carbonates. Depending on the chemistry of the cement paste, KOH, NaOH, and $Mg(OH)_2$, e.g., may be available to the reaction with CO_2. See [Ste00], e.g., for a short account of the corresponding carbonation reactions.

4.2.3 Production of moisture by the carbonation reaction

Besides calcium carbonate, water is produced by the carbonation reaction. In general, a mole ratio of 1:1 of *water released* to *carbon dioxide reacted* is assumed. This water joins the amount of water that is already present in the concrete sample from mixing and curing. Under natural conditions, the low reaction gives the released water enough time to diffuse and leave the specimen (if we assume a lower RH level outside the sample). Therefore, if the structure is sheltered from rain, after a long-term carbonation process the sample will be almost completely dried out. In accelerated tests, when a comparable depth of carbonation is reached, the humidity is still very high. This simply suggests that the humidity does not have sufficient time to leave the sample. At the initial stage, this can even lead to large moisture gradients or a *layer of water* near the exposed surface where the pores are almost saturated. This was particularly observed via numerical simulations in [MPMB05]. Figure 1 shows examples of moisture profiles within a concrete sample during an accelerated test (left) and under natural conditions (right). In the accelerated setting, the moisture concentration exhibits significantly larger values in the already carbonated zone. Similar moisture profiles were also obtained by simulations in [IMS04] and [BS04], e.g.

Figure 1: Numerical prediction of moisture profiles under accelerated and natural conditions. Left: Accelerated test, $CO_2 = 50\%$, RH = 65% (cf. [PVF89]). Right: Natural test, $CO_2 = 0.03\%$, RH = 78% (cf. [Wie84]).

Consequently, the carbonation process becomes slower as the gaseous CO_2 is hindered to progress to the reaction zone. This feature was also reported in [IMS04, Ish05] based on numerical simulations, and experimentally in [SAC03] by measuring the weight changes during carbonation. At a later stage, this water layer may be reduced due to evaporation from the surface of the specimen. Cf. [IMS04], an opposite effect may then occur as a larger amount of water has been stored inside the concrete specimen. Such humidity may facilitate the bulk carbonation reaction by offering a proper reaction medium, hence probably depleting more $Ca(OH)_2$. The saturation of pores due to water released by carbonation is mentioned by various authors, for instance [Cha97, SSV95, Ver58, CSH05]. See also [Par92, GK03, Mun04] for some discussions on the modelling of moisture in concrete and/or the complex inter-dynamics between moisture effects and the chemistry of carbonation.

4.2.4 Effects of heat production by carbonation

It was reported (cf. [CSH05], e.g.) that the increase in $CO_2(g)$ concentration increases the production rate by carbonation. Moreover, when 100% $CO_2(g)$ is used, the heat generated during reaction (about 74 kJ/mole) is so great that a premature drying of samples occurs, and hence (probably) not all the available calcium hydroxide is converted into calcium carbonate. Such a premature drying does not occur when the sample is exposed to natural conditions. Cf. [Cha99], e.g., the solubility of CO_2 in pore water, the production terms by the reactions, and the diffusivity of gaseous CO_2 are also strongly affected by variations in the temperature field. See also [FB90] or any other textbook on physical chemistry. The thermodynamical scenario at the micro-meso scale and its effects on the processes holding at the macroscale is too complex to be included here. A critical view on the mass-balance models (of moisture and involved chemical species), which account for non-isothermal conditions at the pore level and then at the macro level, is done in [BBS97], e.g. The temperature variations play a role in the models of cabonation described in [SSV93, Ste00], e.g.

4.2.5 Leaching of alkaline substances

Calcium hydroxide is one of the main products of the hydration reactions in concrete with Portland cement. It is also one of the more soluble phases of the hydrated parts. The influence of calcium hydroxide dissolution combined with leaching of the hydroxide and calcium ions from the pore water (if the sample is stored in pure water) leads to significant changes in the transport properties of the material. Note that, cf. [MBSM01], e.g., the leaching of calcium hydroxide usually increases the porosity of the concrete. This issue is also strongly related with the very long term durability of nuclear waste disposals. The existing literature on the latter subject is huge. We only refer to [Tor04] and the references therein. For details on modelling the basic mechanisms on which the leaching of $Ca(OH)_2$ relies, see [Mai99, MU01, Kro95, Joh98, Bun94, BS04, Sch76], e.g.

Concerning the carbonation prediction problem, it is reported (cf. [GSK04], e.g.) that the pore water composition differs essentially when natural exposure conditions apply compared to the accelerated case. Note also that in the derivation of the standard-$\sqrt{t}$-law (1) the transport of $Ca(OH)_2$ has been neglected. These facts indicate that the influence of leaching may not be comparable in accelerated and natural settings. Nevertheless, it is also reported that if carbonation takes place, then the tendency of the available $Ca(OH)_2$ to leach out by dissolution is essentially diminished. More on the interplay between carbonation, dissolution, and leaching of $Ca(OH)_2$ is dealt with in [GSK04, GGS$^+$04] as well [BKM03b, BKM03a, MB04b, GM03, MB04a], e.g.

Related issues are: the leaching of $CaCO_3$, drying/wetting cycles, the effect of a sealant, and the type of boundary conditions for $Ca(OH)_2$.

4.2.6 Resistance to exchange with the environment

The various mechanisms by which the concrete specimen interacts with the surrounding environment are not quite clear. For a chemical species in the gaseous phase (such as $CO_2(g)$, e.g.) a Dirichlet boundary condition may describe the mass transfer at the exterior surface quite well. However, for moisture the situation can be rather complicated. See, e.g., [Gru97] and [Gru00]. Cf. [GK03], under specific conditions the drying of the concrete can become controlled by evaporation and diffusion of water vapour through a thin boundary layer near the exposed surface. Note that if a Robin boundary condition is used instead of a Dirichlet one, the classical derivation of the $\sqrt{t}$-law (for instance, via the Green's function technique for linear diffusion equations) leads to different results. In some cases, it may become reasonable to describe an accelerated test with a different type of boundary condition than a natural test.

4.2.7 Ambient moisture and temperature variations

In an outdoor scenario, the concrete sample is exposed to variations in the ambient humidity and temperature. The temperature is important as almost all relevant transport and reaction model parameters as well as absorption isotherms depend on a local thermic equilibrium. See [Ste00, Bun94, Sis04], e.g., for some details. Essentially varying the temperature field, it may occur that gradients of temperature start developing into the material. As a result of this, a heat equation, Soret and Dufour effects, and other specific phenomena couple with the reaction-transport part. Models for non-isothermal carbonation are considered in [BW86, HRW83, SSV93, SSV95, SV04, Ste00, Isg01], etc. The effect of seasonal humidity variations on the progress of the carbonation front are numerically investigated, for instance, in [Ste00, MPMB05]. The influence of humidity has been already discussed in sections 4.2.3 and 4.2.6. Very high as well as very low humidity levels are supposed to slow down the advancement of the front. The accelerated experiments are often performed at a fixed humidity level between 50 and 70%. As an example for a natural setting, in the north of Germany a varying humidity between 70 and 90% is measured. For most of the models described in section 3.1 it is not clear if and how a comparison can be done. In case of models that account for different moisture values a varying ambient humidity is usually replaced by its average in time (cf. [Arf98], e.g.).

Related aspects are: periodic vs. constant inputs, superposition of two or more time-periodic inputs profiles at the outer boundary (summer vs. winter, day vs. night, etc.).

4.2.8 Effect of precipitation (rainfall, e.g.)

If the concrete under natural conditions is not sheltered from precipitation, the results are even harder to compare to an accelerated setting. In a 40-months test, Houst and Wittmann [HW02] observe a significantly deeper CO_2-penetration at faces of a concrete sample which are sheltered from rain in comparison to faces which are directly exposed. See also the experiments by Wierig [Wie84]. It is assumed (cf. [Bun94, Cha99], e.g.) that due to rainfall the pores near the surface are completely saturated with water such that no CO_2 transport can happen. Consequently, the carbonation progress is interrupted by *drying periods* of a characteristic length. The Bakker model [Bak64] tries to account for this site-dependent effect.

5 Suggestions and strategies

In the previous section, a preliminary list of mechanisms has been discussed that usually complicate any interpretation of the carbonation process. Hence, they can lead to highly different results of tests under natural and accelerated conditions. We note that none of the existing models can account for *all* of these effects. This leads to essential limitations in the interpretation of accelerated tests results.

Further progress in the prediction of the carbonation penetration based on accelerated tests can be achieved following different strategies. We note some points which seem promising and partly necessary:

1. More experiments are needed in order to reach a better understanding of the carbonation process under various exposure conditions. In particular, experimental data, which refer to one concrete type, is needed for a variety of CO_2-concentrations and RH levels. Besides carbonation penetration depths, the measurements should also provide concentration profiles of CO_2, $CaCO_3$, and alkaline species for different times[5]. This lack of useful information is specifically emphasised by Andrade et al. in [SAC03].

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[5] *Four* experimental points in the *penetration depth vs. time* curves contain almost no information about the carbonation process. If the whole carbonation process would be a purely diffusive process, then the four points might suffice. Here this is not the case. Much care has to be taken in setting up carbonation tests. For instance, the experimental points to be measured should be related to the number of free parameters defining the whole process.

2. Some of the limitations of existing explicit laws for predicting the carbonation penetration depth can be circumvented by means of mathematical modelling. For instance, Bakker's model is an approach to incorporate moisture effects, at least to some extent. Asymptotic studies can bring some more insight on the dynamics of the reaction layers (or zones) and their penetration into the material (see [BS00, Mai99], e.g.) and so on. These layers may refer to the carbonation reaction or to something else, like dissolution/precipitation reactions, e.g. Nondimensionalisation and appropriate scaling of large models are useful tools to reduce the number of involved model parameters. They can provide a basis to derive asymptotic solutions of simple models. The derivation of the relation (2) can serve as a basis for alike investigations. It might also be fruitful to base on the moving-boundary models in [BKM03b, BKM03a].

   Surely, such asymptotic formulas can only be valid to a certain extent. They usually provide only a particular view (depending on one very small or very large parameter) on the involved processes. Nevertheless, they can help understanding the interconnection between several parallel processes. In cases where no analytical solution can be given, an asymptotic approximation may be an appropriate tool to check the correct behaviour and sometimes the accuracy of the numerical solution.

3. To obtain precise quantitative predictions, the use of numerical implementations of extensive theoretical models (like those from [SV04, Ste00, BKM03a, Gru00, MPMB05, PMMB05, SMB05], e.g.) is inevitable. Reliable methods have to be developed to fit the respective models with accessible data from accelerated tests. This leads to classical parameter identification problems. In most of the cases, such problems are ill-posed, and therefore, a conceptually simple identification procedure is not always possible. One way to deal numerically with such issues is offered by various existing shooting strategies. However, if such strategies are to be applied to large systems of nonlinear differential equations, many technical difficulties are expected to occur.

4. It has to be mentioned that the purely macroscopic models are not capable to include all microscopic effects described in section 4.2. Therefore the use of models incorporating microstructure effects can yield much more accurate prediction results. In addition, the mathematical tool of homogenisation can help identifying parameters in macromodels. In particular, the structure of the diffusion constant or *diffusion tensor* strongly depends on the local microstructure and is one of the key parameters for predicting the carbonation depth.

6 Summary

A review of extrapolation strategies from accelerated carbonation tests is presented. A set of possible limitations is summarised. These are theoretically predicted and/or experimentally observed. It is pointed out that some of the issues are inevitable, but some other could be circumvented by means of modelling. This note has a preliminary character. The elaboration of extrapolation strategies is planned in future work, for instance based on shooting strategies. The review of the problems in section 4 and the list of relevant references are also far from being complete.

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