

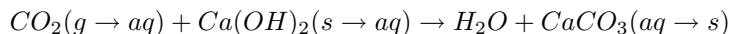
# Chapter 1

## Introduction

### 1.1 A Moving-Boundary Problem: the Carbonation of Concrete

The thesis deals with the modeling, analysis and simulation of the progress of the carbonation reaction in concrete-based materials, see section 2.1 for a detailed statement of the problem. We describe the evolution of the carbonation front separating the uncarbonated region from the carbonated part of a partially saturated concrete sample via two conceptually different moving-boundary problems (mbp), which we refer to as *moving-interface (carbonation) models*. This new modeling approach yields coupled semi-linear systems of reaction-diffusion equations acting in two-phase domains. They either present a moving sharp interface (the model  $P_\Gamma$ ) or two moving internal reaction layers (the model  $P_{2\epsilon}$ ). *Non-local* kinetic laws are used to model the advancement of the internal interface or layer that separates the different domains. We derive such laws via first principles for simple geometries using the physicochemistry of the problem. Since the velocity of the reaction interface or layer is described by alike relationships, the accuracy of the prediction is based on them, but also on a proper definition of the reaction front position. The final scope of the models is to serve as forecasting tools for estimating the initiation of corrosion in concrete. Further comments on these formulations can be found in chapter 2 as well as in [BKM03a, BKM03b, MB04a, MB04b], e.g.

The solution of our moving-interface carbonation models consists of determining the concentration fields of the active species (reactants and products) entering the carbonation reaction



and the position of the moving *front*<sup>1</sup>. While we confine our study to the case of one-dimensional geometries, the theory presented here is comprehensive and includes global existence, uniqueness, continuity with respect to data and model parameters and other qualitative properties of the solution, and also an algorithm to compute the solution numerically. The analytic results ensure the

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<sup>1</sup>In this work, the word *front* has a twofold significance. It either means *sharp-interface* or *thin layer*.

well-posedness of our models and are useful for the model verification. We perform numerical simulations in order to illustrate the qualitative properties of the solution and recover measured penetration depths from a couple of accelerated and natural carbonation tests, which are concisely described in appendix C.

A large numbers of studies on the one-dimensional Stefan problem were devoted to classical and weak solutions in the case of scalar non-linear parabolic equations with various equilibrium or non-equilibrium conditions at the moving interface. See, for instance, the monographs by Rubinstein [Rub71], Friedman [Fri88], Meirmanov [Mei92], Cannon [Can84], Hill [Hil87], Vuik [Vui93] and the references therein. Systems of moving-boundary problems have been dealt with by several authors, for instance, in [FH96, FRZ95, BR97a, BR97b, CCF85]. The methods in [FH96, FRZ95, CCF85, PK96] yield classical solutions. Since we aim at extending the analysis to tackle quasilinear reaction-diffusion systems to which we might later also add the partial differential equations (pdes) describing the mechanics of the concrete, alike methods can not be exploited in our context. We are primarily interested here in proving the well-posedness of weak solutions to our models. Specifically, for systems of pdes maximum and minimum principles are generally not available. Therefore, other methods have to be applied to gain the positivity and maximum estimates of the solution. Conceptually close to our setting are [Paw90, CHS90, BR97a, BR97b, BDJR98, CR05], e.g. In these papers, only one-phase systems of pdes are dealt with, and hence, the supplementary interface conditions are rather non-sophisticated kinetic laws. An example of a homogeneous two-phase moving-boundary problem with a kinetic condition at the moving interface is treated by Visintin in [Vis87], e.g. At the practical level, scenarios from Fasano *et al.* [FMP86] (penetration of solvents into polymers), Ortoleva [Ort94] (fast reaction – slow diffusion scenarios in geo-chemistry), Froment and Bischoff [FB90] (noncatalytic gas-solid reactions with large Thiele moduli) and Caboussat and Rappaz [CR05] (free-surface flow model of Burgers-Stefan type), e.g., are conceptually related to this work. On the other hand, at the technical level, at least in what the proof of the local existence and uniqueness of solutions is concerned, the contributions by Böhm and Rosen [BR97a, BR97b] prove to be important for choosing the strategy of construction of the fixed-point operators.

Of a particular interest for us are the papers by Souplet *et al.* [SGT01] and Fila and Souplet [FS01]. They succeeded to complete the study of the well-posedness and established the global behavior of classical solutions for a one-phase Stefan-like problem with super-linear production term (i.e. the right-hand side of the pde has a power-law structure with super-unitary exponent) and Dirichlet-Neumann boundary conditions. They were able to classify the behavior of the global solutions as fast and slow solutions (in a certain sense) taking explicitly into account the size of the exponent in the production term. A similar working program for investigating the effects of the production terms by reaction on the transport part may also be planned for our moving interface models, see section 3.6. However, some fundamental qualitative features have to be firstly ensured in order to gain a basic analytic understanding of the proposed models. This is the scope of chapter 3.

To perform the simulations in chapter 4, we use a front-fixing approach (cf. Crank [Cra84]) and a vertical method of lines (MOL) scheme, in which the spatial discretization has been constructed on a fixed grid by means of piecewise linear finite elements. Some preliminary numerical investigations of models  $P_{\Gamma}$

and  $P_{2\epsilon}$  have been reported in [BKM03a, BKM03b, MB04b], e.g. For related numerical studies, the reader is especially referred to [BDJR98, SGS05], but also to [BK99, SS97, Nar06], e.g.

In the present work, we take the following steps:

- (1) Develop moving-boundary models for concrete carbonation (e.g.  $P_\Gamma$ ,  $P_{2\epsilon}$ );
- (2) Prove those basic qualitative behaviors which can ensure the well-posedness (in a certain sense) of the models proposed in (1);
- (3) Acquire an appropriate picture about how close the proposed models [from (1) satisfying the properties declared in (2)] can recover realistic scenarios and identify the most influential model parameters.

We intend to point out that the models presented in this thesis are a reliable working alternative<sup>2</sup>. At this stage, the following questions are important:

- (Q1) Under which restrictions on the size of the material parameters, initial and boundary data is the well-posedness of the moving interface carbonation models ensured? Are these restrictions physically acceptable?
- (Q2) Do the active concentrations remain positive and bounded from above along the existence time interval?
- (Q3) Do the proposed models recover typical patterns usually shown by concrete carbonation in the frame of accelerated tests and tests under normal outdoor exposure conditions?

## 1.2 Outline of the Thesis

Each chapter deals with distinct matters. We made them self-contained so that they can be read separately. Appendices A and B complement the exposition. We briefly describe the contents of the chapters:

Chapter 2 introduces the model problem that we are dealing with. The bulk of the chapter presents the modeling of various aspects concerning the concrete carbonation: precipitation and dissolution reactions, reaction-induced changes in porosity, transport of moisture, e.g. We develop model equations that may constitute a prototype of some reaction-diffusion scenarios that can take place in many reactive porous materials. The main modeling results are formulated in sections 2.3 and 2.4, namely *the moving-interface models*  $P_\Gamma$  and  $P_{2\epsilon}$ .

Chapter 3 is an exposition of the well-posedness of global weak solutions to the moving-boundary problems  $P_\Gamma$  and  $P_{2\epsilon}$  introduced in the previous chapter. This constitutes the bulk of the thesis.

Chapter 4 presents an elementary treatment with finite elements of one-dimensional one-phase and two-phase systems of weakly coupled parabolic equations having several moving internal reaction layers. Auxiliary results are presented in Appendix A. Numerical simulations illustrate the typical behavior of concentrations and interface position for our models when various model parameters are drastically changed.

A review of results and a summary of conclusions are drawn in chapter 5.

The chapters begin with an overview of the subject matter, together with an orientation as to how the topics presented are related to those in previous

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<sup>2</sup>See section 2.1.2 for a review of earlier modeling approaches of concrete carbonation.

and subsequent chapters. Except for chapters 1 and 5, they end up with a section entitled *Notes and Comments*. The purpose of such a section is to briefly comment on topics that selectively complement the chapter. This is not meant to be exhaustive but rather offer a glimpse on some closely related problems. The choice of topics is based on our personal taste. Within this frame, we collect a few ideas, open problems and methods of analysis in simple (often *pathological*) cases, rather than on pursuing each problem to its limits. Some additional references to related matters are also added. Many footnotes accompany the text. Their goal is to additionally comment on some issues of local importance. Nevertheless, the footnotes and the Notes and Comments sections are not essential for the logical understanding of the text. References to the literature are given at the end. The numbering of theorems, lemmata, formulae, etc. is made for each chapter separately. When a reference is made to the current chapter or to a different one, this is explicitly stated.

**Key Words and Phrases:** Moving-boundary problem, reaction-diffusion equations, weakly non-linear parabolic systems, *a priori* estimates, well-posedness, porous media, corrosion, phase transformations in solids, concrete carbonation

**MSC (2000):** 35 R 35, 35 K 57, 35 K 45, 35 K 60, 35 B 50, 35 D 05, 35 B 30, 74 F 25, 74 N 99

## Chapter 2

# Moving-Interface Carbonation Models

*Orientation:* The goal of this chapter consists of formulating the equations that govern the concrete carbonation process at the *macroscopic scale*. In section 2.1, we present some of the specifics, while the basic geometry of the setting we are dealing with is described in section 2.2.1. Based upon several modeling assumptions, which we mention ahead step-by-step, we present the general reaction-diffusion model (see the subsections of 2.2). The main results of this chapter are the moving-interface models  $P_\Gamma$  and  $P_{2\epsilon}$  as well as the intermediate formulation  $P_{\Gamma\epsilon}$ , see sections 2.3 and 2.4. The models represent a *new approach* to the study of the concrete carbonation problem and partly rely on the preliminary reports [BKM03a, BKM03b, MB04b, GM03] and [MB04a]. Section 2.5 contains further directions and open problems concerning the modeling part.

## 2.1 Problem Statement

### 2.1.1 Comments on the Physics of the Situation

In all carbonation scenarios, gaseous carbon dioxide is assumed to be supplied from an inexhaustible exterior source to the concrete sample. It is well-known that carbon dioxide entering the non-saturated concrete sample through the air parts of the pores dissolves into the pore water and forms carbonic acid. Due to the low stability of the latter product and availability of calcium hydroxide in solution, the calcium carbonate is formed as a result of the carbonation reaction. This product of reaction is low soluble in the pore water. Its precipitation is assumed to occur quickly once a critical degree of super-saturation is attained. Water represents the second product of the reaction. Its precise role in the overall process is not quite clear. At one hand it provides a medium favorizing reaction, on the other hand, the water either drying out or wetting the sample fills the void space of the pores with the clear tendency to saturate the material. It has been shown via simulations (see [MPMB05, MMP<sup>+</sup>05], e.g) and by experiment (see [IMS04], e.g.) that the water produced by carbonation can locally form a barrier for  $CO_2(g)$ . This may act as an obstacle with respect to the ingress of  $CO_2(g)$ . Such a barrier-like pattern can strongly influence the

extrapolation of results from the accelerated test to the natural exposure case. In the civil engineering community, there is neither a general strategy, nor a common agreement on how to deal with such nonlinear phenomena [KHG<sup>+</sup>95]. The complex reaction pathway, the complexity of the transport mechanisms for chemical species in non-saturated porous materials, together with the role of water in concrete, have to be taken into account in order to obtain a quantitative description and a reliable forecast of the time and space evolution of concentrations. It is therefore necessary to start with a simplified approach of the problem. Our modeling strategy relies on the *moving-interface methodology* and it is explained in sections 2.3 and 2.4.

### 2.1.2 Earlier Studies

Several experimental studies addressed the problem of carbonation of concrete-based materials. Up-to-date information about what is known in the field of concrete durability with respect to the carbonation process is collected in the survey paper by Chaussadent [Cha99]. For detailed literature studies concerning the carbonation process (and some closely related matters), the reader is referred to the dissertations by Kropp [Kro83], Bier [Bie88] and Bunte [Bun94], e.g. Recent completions are added by the contributions of Steffens [Ste00], Sismophon [Sis04], Oisgor-Burkan [BI01] and Maekawa and Ishida [IM01]. Our standard references of published data regarding long-time carbonation tests under various natural exposure conditions are the report by Wierig [Wie84] and the thesis by Bunte [Bun94]. In order to be able to see a certain progress of the process in a short time interval (at the laboratory time-scale, e.g.), several types of accelerated tests have been proposed [Cha99]. They all aim to determine the penetration of the carbonation front within a few days or weeks. A concise description of a typical accelerated test setup is given in appendix C.

Particularly important for our investigation are the papers by Houst and Wittmann [HW02], Houst, Roelfstra and Wittmann [HPR83], Saetta, Vitaliani and Schrefler [SSV93, SSV95, SV04], Steffens, Dinkler and Ahrens [SDA02]. They are all concerned with modeling and simulation issues. The authors tune their models in order to fit measured penetration curves in case of various boundary conditions and types of cements. Another step towards the understanding of the overall process is done by the dimensional and asymptotic analyses by Papadakis, Vayenas, and Fardis in [PVF89] and in a series of subsequent papers. The thesis by Tuutti [Tuu82] and the paper by Brieger and Wittmann [BW86] are conceptually close to our moving-interface approach. Tuutti is the first one who used the moving-boundary methodology to model the carbonation of concrete. He basically frames a simplified carbonation scenario<sup>1</sup> into the classical setting of the two-phase Stefan problem. Using the Neumann solution to this problem (cf. [Cra75], section 13.2.2) he is able to calculate the reactants concentration as well as the position of the sharp interface that separates the two reactants. As a straightforward consequence, he obtains *analytically* that the interface between completely carbonated parts and non-carbonated parts behaves like  $\sqrt{t}$  for sufficiently large time  $t$ . This was a novelty at that

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<sup>1</sup>Two model assumptions have to be recalled here: (1)  $CO_2$  and  $Ca(OH)_2$  are segregated species whose concentrations are vanishing at the separating interface; and (2) There are no volume or surface productions by carbonation, the carbonation reaction being tacitly supposed to happen instantaneously at the separating sharp-interface.

time, since all *prior*  $\sqrt{t}$ -laws for predicting the concrete carbonation penetration were based exclusively on fitting arguments. Brieger and Wittmann incorporate the carbonation problem into the framework of the two-phase Stefan problem, too. The main difference compared to Tuutti's approach consists of the presence of productions by reaction across the separating interface. They prescribe Rankine-Hugoniot jump conditions along the reaction interface for all active concentrations and point out that all involved concentrations and the respective Fickian fluxes may have jumps across the reaction interface. Unfortunately, they omit to impose a second condition across the moving interface, and hence, their moving-boundary models become mathematically ill-posed.

There are few types of PDE models describing the concrete carbonation<sup>2</sup>:

- (I) The active concentrations (i.e. reactants and products) are present everywhere in a volume control, say  $\Omega$ , at all times.
- (II) The reactants are *completely separated* by a thin front, say  $\Gamma(t)$ , in which they may coexist. One reactant lives in  $\Omega_1(t)$ , while the second one in  $\Omega_2(t)$ . The regions  $\Omega_1(t)$  and  $\Omega_2(t)$  are disjoint parts of  $\Omega$ , but have a common boundary.
- (III) The reactants are separated by a more or less thin front in which they may coexist. Additionally, a secondary reaction may happen as soon as dissolution of the alkaline species acts in the product zone  $\Omega_1(t)$ .

We refer to models of type (I) as *isolines* or *mixed models* and the models of type (II) as *moving interface*<sup>3</sup> or *segregated models*. Models of type (III), which we call *secondary carbonation models*, are a special class of models of the type (II).

Almost all existing carbonation models are of type (I) and are mainly based on linear or semi-linear systems of parabolic pde's with volume production terms. An exception from the rule are some of the models for the moisture behavior in unsaturated concrete fabrics<sup>4</sup>. Although isolines models are more realistic, moving-interface models may represent a good approximation. This is especially true for accelerated carbonation tests but also for *some* of natural carbonation scenarios [PVF89, Bun94] for various types of cements. The condition for occurrence of sharp fronts is that the process is in its fast reaction/slow diffusion regime, see appendix A.

The carbonation process is framed within the most important durability issues of concrete structures exposed in aggressive environments [JKS96, Mar01], e.g. In combination with a few other durability issues, it is sometimes called the *cancer of the concrete*. We approach the carbonation problem via models of type (II) with the hope to contribute to a better understanding and better prediction of the overall process. This should offer complementary information to that obtained by employing models of type (I), [MPMB05, PMMB05, SMB05]. At this stage, it is not at all clear which type of model covers the reality the best.

<sup>2</sup>This is not the unique way to classify the carbonation models. A different classification is given in [MMP<sup>+</sup>05], e.g.

<sup>3</sup>The word *interface* refers to the *location* where the carbonation reaction takes place. This is most likely a reaction zone and, in ideal cases only, it might be a surface. Generically, we call all our moving boundary formulations *moving-interface carbonation models*.

<sup>4</sup>Some of the moisture potentials can lead to second-order hyperbolic equations.

It seems that all of (I)-(III) equally requires attention. Within this frame, we focus on models belonging to the classes (II) and (III).

## 2.2 The Reaction-Diffusion Problem. Modeling Assumptions

We prepare the formulation of the equations governing the carbonation process at the *macroscopic scale*. The step between explaining the physical and chemical issues, which are relevant at a microscopic scale, and writing down the equations at the macroscopic level, is usually done via an averaging argument (see, for instance, [Bea72, Kna91, CD99, Hor97], etc., but also [Pet06, Mei06, SMB99] for applications in case of cementitious materials). Our explanations regarding phenomena taking place at the pore level only intend to give some motivation to the various production terms and rival effects at the macro-scale. Proving all statements by an homogenization approach represents a tedious task by itself and is beyond the scope of this work. Questions of primary interest are: *How can one define the position of the reaction front? How do the concentrations and the reaction front (in one of its forms sharp-interface, thin layer or thick zone) evolve in time? Which mechanism drives the front?*

### 2.2.1 Basic Geometry. Choice of Porosities

We consider a part of a concrete member that is exposed to ingress of gaseous  $CO_2$  and humidity from the environment. Fig. 2.2 shows a typical control volume (box A) in such a structure. We denote by  $\Omega$  the whole box A (or part of it) for which we model the carbonation process under natural exposure conditions. If we refer to an accelerated test, then the geometry we have in mind is depicted in Fig. 2.3 and  $\Omega$  is now part of box B.

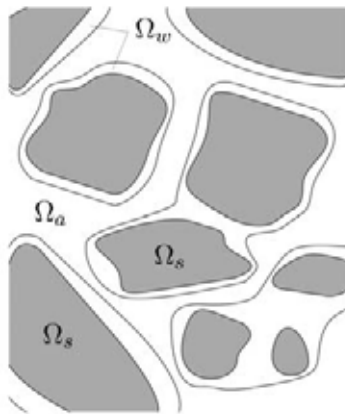


Figure 2.1: Concrete as a multiphase material, [Mei06].

The typical situation in the process of concrete carbonation can be summarized as follows: Generally, the concrete matrix is made of a mixture of water,



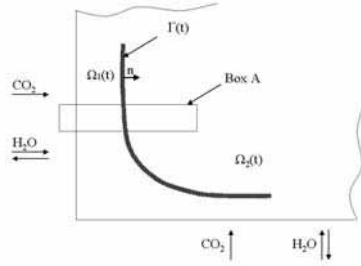


Figure 2.2: Typical corner of a concrete structure. The box A is the region to which our model refers when dealing with natural exposure conditions.

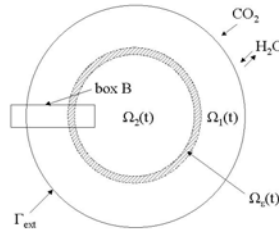


Figure 2.3: Cross section of a cylindrical concrete sample. The grey area indicates a zone  $\Omega_\epsilon(t)$  of steep change in pH.  $\Omega_2(t)$  is the uncarbonated zone.  $\Omega_1(t)$  is the partially carbonated zone,  $\Gamma_{\text{ext}}$  - the exterior boundary. The box B is the region to which our model refers when discussing the accelerated carbonation test.

cement<sup>5</sup> and aggregate. Such mixtures, once they are hardened, have a definite porous structure. The grains (gravel, sand, etc.) or particles have different sizes, held together by compression and cementing material and form a multiphase composite with complex chemistry, see Fig. 2.1. To describe reaction-diffusion processes in such multiphase materials, we make use of a few specific notations and definitions. Let  $\Omega(t)$  denote a representative control volume within the concrete sample at the time  $t \in S$ , where  $S$  represents a given time interval. The dependence of  $\Omega$  on the time  $t$  shows that possible changes in the shape and volume could be allowed. However, within the frame of this thesis, the size and shape of this region is assumed to be constant. Therefore, we account for  $\Omega = \Omega(t)$  for all  $t \in S$ . The region  $\Omega$  consists of two distinct parts  $\Omega_p$  and  $\Omega_s$ . The part  $\Omega_p$  represents the inner pores space, and  $\Omega_s$  is the part occupied by the consolidated aggregate and mortar.

<sup>5</sup>We have in mind the application of the moving-interface models on concrete-based materials containing ordinary Portland cement. For other type of cements, the whole setting has to be extended to account for more carbonation reactions and for additional competitive chemical effects, see [PMMB05], e.g.