Mathematical issues concerning evolving sharp-reaction interfaces in non-saturated reactive porous materials

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Supported by DFG-SPP1122
Prediction of the Course of Physicochemical Damage Processes Involving Mineral Materials

Eindhoven, May 2007
Modeling corrosion of concrete via *moving reaction interfaces*
Outline of the Talk

Modeling Carbonation via Moving Interfaces
  - Basic Geometry
  - Primary and Secondary Carbonation Effects
  - Transport and Production Terms
  - Moving-Interface Carbonation Models

Analysis (Special Cases)
  - Fixed-Domain Formulation
  - Main Results: Local and Global Well-Posedness; Regularity; Useful Bounds

Numerical Simulation (Special Cases)
  - Scaling of the Moving-Boundary Models
  - Simulation Results. Validation of the Models

Summary. Further Research. Open Problems
The *moving-boundary problem*

Industrial need: Prediction of the lifetime of concrete-based materials!

- What means carbonation of concrete?
- *Why and how* is a moving-boundaries (interfaces) approach applicable?
- Which mechanism drives the front position?
- Aims:
  - better understanding of the process
  - quantitative prediction
Carbonation of concrete

Reaction of $\text{CO}_2(g)$ from the environment with $\text{Ca(OH)}_2$, KOH, NaOH, Mg(OH)$_2$, C-S-H and C-A-H phases, $\text{C}_2\text{S}$, $\text{C}_3\text{S}$, etc.

- The concrete sample is *sufficiently* wet
- $\text{CO}_2(g)$ penetrates the concrete via the air phase and dissolves in the pore water ($\text{CO}_2(aq)$)
- **Reduced scenario**: Here (!) $\text{CO}_2(aq)$ reacts in the aqueous phase with $\text{Ca(OH)}_2(aq)$ available by dissolution from the pore matrix

\[
\text{CO}_2(g \rightarrow aq) + \text{Ca(OH)}_2(s \rightarrow aq) \rightarrow \text{H}_2\text{O} + \text{CaCO}_3(aq \rightarrow s)
\]
Specific goals:

- Prediction of the carbonation penetration depth
- Estimation of the final time of the process

The tools are our \textit{(newly developed)} carbonation models:

- moving sharp-interface model
- moving reaction-layer model
- moving two-reaction zones model
- isolines model [with \textit{reduced} and \textit{extended} chemistry]
  (carbonation of CH, CSH, C$_2$S, C$_3$S + \textit{concurrent} hydration and pozzolanic reactions)

\textit{The isolines model is used for validation/comparison.}
Basic geometry

Typical corner of a concrete structure.

Cross-section of the sample we deal with.

Our 1D geometry:
What is the carbonation front?

I. Geometrical alternatives?
   (a) The front is thin and can be idealized by a surface $\Gamma(t)$.
   (b) $\Gamma(t)$ is the centerline of a reaction layer $\Omega_\epsilon(t)$.
   (c) Isolines models/the concept of carbonation degree

II. Alternatives employing the chemistry of the sample? (e.g. using the drop in pH or a reactant profile)

Secondary reaction effects!

Each kinetics is proportional to $[\text{CO}_2]^p[\text{Ca(OH)}_2]^q$, $p \geq 1$, $q \geq 1$ (generalized mass-action law).

$u = (u_1, u_2, \ldots)^t$ is the concentration vector and $\Lambda \subset M_\Lambda$ is a set of parameters. Here $\eta = \eta(u, \Lambda)$ is positive, locally Lipschitz and bounded in $u_3$. 
Transport and productions by dissolution/precipitation/Henry-like exchange

Special cases:

- $u_1$ – concentration of $\text{CO}_2(aq)$
- $u_2$ – concentration of $\text{CO}_2(g)$
- $u_3$ – concentration of $\text{Ca(OH)}_2(aq)$, . . .
- $j_i := -D_i \nabla u_i$ Fickian flux of $i$th species
- Exchange at air/liquid interfaces (via Henry’s law)
  \[
  f_{i,\text{Henry}} = \pm P_i \cdot (Q_i u_2 - u_1)
  \]
- Productions by dissolution/precipitation:
  \[
  f_{i,\text{diss/prec}} = \pm S_{i,\text{diss/prec}} \cdot (u_{i,eq} - u_i)
  \]
The reaction-diffusion system in the sharp-interface case

Mass balance of $\text{CO}_2(\text{aq})$ in $]0, s(t)[$:

$$\frac{\partial u_1}{\partial t} - D_1 \Delta u_1 = P_1(u_1 - Q_1 u_2)$$

Mass balance of $\text{CO}_2(\text{g})$ in $]0, s(t)[$:

$$\frac{\partial u_2}{\partial t} - D_2 \Delta u_2 = -P_2(u_1 - Q_1 u_2)$$

Mass balance of $\text{Ca(OH)}_2(\text{aq})$ in $]s(t), L[$:

$$\frac{\partial u_3}{\partial t} - D_3 \Delta u_3 = S_{3,diss}(u_3,_{eq} - u_3)$$

+ PDEs in two phases for moisture + PDE for the precipitating $\text{CaCO}_3$
+ initial and boundary conditions

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Conditions across the moving interface

- Rankine-Hugoniot conditions at $x = s(t)$ for each active concentration:
  
  \[-D_1 \nabla u_1 = s'(t)u_1(s(t), t) + \eta(u(s(t), \Lambda))\]
  
  \[-D_2 \nabla u_2 = s'(t)u_2(s(t), t)\]
  
  \[-D_3 \nabla u_3 = s'(t)u_3(s(t), t) - \eta(u(s(t), \Lambda))\]

- Evolution law for the velocity of the reaction interface:
  
  \[s'(t) = \Psi_{\Gamma(t)}(\eta(u(s(t), t), \Lambda), u_3(s(t), t)), \text{ with } s(0) = s_0.\]
Well-posedness: *local* vs. *global* results

The *working program* is in some sense classical:

(A) *Local* well-posedness of the model:
   - Existence of locally in time positive weak solutions
   - Uniqueness of weak solutions
   - Continuous dependence of the weak solution w.r.t. initial data and model parameters
   - Regularity

(B) Further (practical) estimates:
   - Strict lower bounds on all involved concentrations
   - Lower and upper bounds on the speed of the reaction front
   - Upper bound on the final time of the carbonation process
   - Lower bound on the time needed to initiate corrosion

(C) Now, (A) + (B) $\rightarrow$ *global* well-posedness of the *mbp models*
Fixed-domain formulation. Landau’s trick

*Freeze* the moving boundaries by mapping

\[ \Omega_2(t) \times [0, T] \ni (x, t) \rightarrow (y, t) \in [1, 2] \times [0, T] \text{ via } y = 1 + \frac{x - s(t) - \epsilon/2}{L - s(t) - \epsilon/2}, \text{ e.g.} \]

**Advantage vs. drawbacks:**

\[ v_t + Dv_{xx} = f(v) \text{ in } [s(t) + \epsilon/2, L[ = \Omega_2(t) \]

becomes

\[ u_t + \frac{D}{(L-s(t)-\epsilon/2)^2} u_{yy} + \frac{s'}{L-s(t)-\epsilon/2} yu_y = f(u) \text{ in } [1, 2[. \]

**Geometrical restrictions:**

- \( 0 < s_0 \leq s(t) \leq L^* < L \) for all \( t \in S_T \)
- \( 0 < \epsilon < L - 2s_0 \) *a priori* given.

The *weak formulation* will refer to the fixed domains \([0, 1], [1, 2] \) (say \([a, b]\)).
**Theorem**: Under *some restrictions* on the *model parameters*, *structure of the production terms* and *geometry*, there exists a positive weak solution on a sufficiently small time interval, i.e. \( \exists \delta > 0 \) such that w.r.t. \( S_\delta = ]0, \delta[ \) we have

\[
s \in W^{1,4}(S_\delta)
\]

\[
u \in W^1_2(S_\delta, V, H) \cap [S_\delta \to L^\infty(a, b)]^{nspec}
\]

with

\[
u(0) = u_0, s(0) = s_0,
\]

\[
s'(t) = \psi_{\Gamma(t)}(\eta(u(s(t), t), \Lambda), u_3(s(t), t)), t \in S_\delta.
\]
Estimates (e.g.):

- Positivity/Maximum Estimates: $0 \leq u_i(y, t) + \lambda_i(t) \leq k_i$ for all $y \in [a, b]$, $i = 1, \ldots, \text{nspec}$ a.e. $t \in S_\delta$ (nonstandard)
- Energy Estimates (standard $L^2$-setting)

**Corollary:** Monotonicity of the reaction interface location
The position $s \in W^{1,\infty}(S_\delta)$ of the reaction interface $\Gamma(t)$ is monotonically increasing for a.e. $t \in S_\delta$. 
Construction of the fixed-point operator

Let \( S_\delta = ]0, \delta[, \delta > 0, \sigma > 0 \). Select \((M(S_\delta), \rho)\), where

\[
M(S_\delta) := \{ r \in W^{1,4}(S_\delta) : r(t_0) = \bar{s}_0, r(t) - s_0 \in [0, \delta\sigma],
\]

\[
r'(t) \geq 0 \text{ a.e.} t \in S_\delta, |r'|_{L^4(S_\delta)} \leq \sigma \neq \emptyset
\]

and

\[
\rho : M(S_\delta) \times M(S_\delta) \to \mathbb{R}_+ : \rho(r_1, r_2) = |r_2' - r_1'|_{L^4(S_\delta)} \quad \forall r_1, r_2 \in M(S_\delta).
\]

Solve

\[
\begin{cases}
  s' = F_s(s, u) \quad \text{(A)} \\
  B(s)u' + C(s, s', u, u_y) = F_u(s, u) \quad \text{(B)}
\end{cases}
\]

Set \( T : s_i \in M(S_\delta) \mapsto \text{solution } u_{s,i} \text{ of (B)} \mapsto r_i \in W^{1,4}(S_\delta) \) cf. (A) \((i = 1, 2)\)

Prove:

(i) \( T : M(S_\delta) \to M(S_\delta) \) is well-defined \( \forall \delta > 0 : S_\delta \subset S_T \).

(ii) \( \exists \chi > 0 : \rho(Ts_2, Ts_1) \leq \delta \chi \rho(s_2, s_1) \) with \( \delta \chi < 1, \forall s_1, s_2 \in M(S_\delta) \).

Repeat the procedure on \( S_{2\delta} = ]\delta, 2\delta[, S_{3\delta} = ]2\delta, 3\delta[, \ldots \)

When should we stop?
Stability estimates

The application

\[ \mathbb{H} \times W^{1,2}(S_\delta)^{\text{spec}} \times M_\Gamma \times M_\Lambda \times \cdots \rightarrow W^1_2(S_\delta, \mathbb{V}, \mathbb{H}) \times W^{1,4}(S_\delta) \]

which maps

\[ (u_0, \lambda, u_{eq}, k, \ldots) \rightarrow (u, s) \]

is Lipschitz continuous, i.e. \( \exists c > 0 \) such that

\[ \|u_2 - u_1\|_{W^1_2(S_\delta, \mathbb{V}, \mathbb{H}) \cap L^\infty(S_\delta, \mathbb{H})}^2 + \|s_2 - s_1\|_{W^{1,4}(S_\delta) \cap L^\infty(S_\delta)}^2 \leq c \left( \|u_{0,2} - u_{0,1}\|_{\mathbb{H} \cap L^\infty(a,b)}^{\text{spec}}^2 + \|\lambda_2 - \lambda_1\|_{W^{1,2}(S_\delta)^{\text{spec}} \cap L^\infty(S_\delta)^{\text{spec}}}^2 + \right. \]

\[ \left. + \|u_{eq,2} - u_{eq,1}\|_{M_\Gamma \cap L^\infty(S_\delta)}^2 + \max_{M_\Lambda} |k_2 - k_1|^2 + \ldots \right) , \]

where the choice of \( c \) depends on the maximum estimates and model parameters.
Global solvability of the MBP

**Working Program:** local solutions on $S_\delta$ to global solutions on $S_{T_{\text{fin}}}$ via additional estimates (similar arguments as for ode’s)

*Example of estimates:*

(i) strict lower bounds on active concentrations: $u \geq u_{\text{LOW}} > 0$

(ii) on the interface position and its speed: $\eta_{\text{min}} < s'(t) < \eta_{\text{max}}$ ($t \in S_\delta$)

(iii) on the final time of the process: $\frac{L_0 - s_0}{\eta_{\text{max}}} < T_{\text{fin}} < \frac{L_0 - s_0}{\eta_{\text{min}}}$

Here $\eta_{\text{min}}$ and $\eta_{\text{max}}$ denote uniform lower and upper bounds of $\Psi_{\Gamma(t)}(\cdot)$.

- By (iii), we uniquely extend the solution up to $S_{T_{\text{fin}}}$.
- Input from analysis into modeling: revisit (ii) and (iii) !!!
Nondimensionalization of the models

- support for numerics
- distinguish between large and small contributions
- supplementary bonus

In our case, bonus means:

1. \( s' \sim \Phi^2 \),
2. \( \epsilon \sim \frac{1}{\Phi^2} \),

where

\[ \Phi^2 := \frac{\tau_{\text{diff}}}{\tau_{\text{reac}}} \]

is Thiele modulus (or 2nd Damköhler number). Here \( \Phi^2 \gg 1 \) → fast reaction vs. slow diffusion scenario...

Special case (for further work):

- Study \( \epsilon \to 0 \), i.e. shrink the layer \( \Omega_\epsilon(t) \) to \( \Gamma(t) \) (disappearance of the mushy region)
Simulation of carbonation penetration in concrete: case studies

We focus on two different situations:

▶ accelerated carbonation tests (short term tests, most of the data is fairly well controlled)
▶ natural carbonation tests (long term tests)

Main output: **Penetration depth vs. time** curve!
Typical concentration profiles. Penetration depth vs. time

$\text{CO}_2(\text{aq}), \text{Ca(OH)}_2(\text{aq}), \text{CaCO}_3(\text{aq})$ profiles vs. position in the sample. Each curve refers to time $t = i$ years, $i = 1, \ldots, 18$. Interface position vs. the experimental points “◦” after $T_{\text{fin}} = 18$ years of exposure.
Internal layer formation in the carbonation problem (isolines approach). Both $\text{Ca(OH)}_2$ and CSH can react with $\text{CO}_2$ to produce carbonates. See S. Meier, M. Peter, A. Muntean, M. Böhmb: Modeling and simulation of concrete carbonation with internal layers. (Chem. Engng. Sci. 62 (2007), 1125-1137)
Water barrier effect

Numerically, we note that the production of water may locally fill air parts of the pores hindering in this way the transport of $\text{CO}_2$. This effect is visible especially in the simulation of accelerated tests.

![Graph showing moisture profile](image1)

Prediction of moisture profiles under accelerated and natural conditions. Left: acc. test, $\text{CO}_2 = 50\%$, RH=65%. Right: nat. test, $\text{CO}_2 = 0.03\%$, RH=78%.

Self-adaptivity around corners

We are interested in capturing effects of the sample geometry on the speed of penetration. In the enclosed figure, we see that around corners the carbonation front moves faster. Tool: Self-Adaptive Finite Element Method

Carbonation attack around a corner: self-adaptive approach

See A. Schmidt, A. Muntean, M. Böhm: *Numerical experiments with self-adaptive finite element simulations in 2D for the carbonation of concrete (2005)* (Simulation with ALBERTA, Transcon/RILEM proceedings (2007)).
Summary. Further research/open problems

Summary

(1) New modeling methodology
(2) Scaling, practical bounds, well-posedness of the models
(3) The models provide results in good agreement with data from accelerated/natural tests.

Further research (Modeling)

▶ improved modeling of \( \text{CaOH}_2 \) dissolution
▶ What can be drawn from the short-time experiments w.r.t. long time ones?
  ▶ qualitative information (ok) / quantitative information (?)
▶ Suggest a carbonation scenario, where a \( t^{\alpha} \)-law is applicable and a correct extrapolation between accelerated and natural information is guaranteed?
Further research (Analysis)

- $\epsilon \to 0$, $\Phi^2 \to \infty$, *slow diffusion* limit(s) ($D_2 \to 0$, $D_3 \to 0$)
- Long-time behavior of concentrations and reaction location
- Stefan-Signorini conditions driving moving interfaces
- Dynamics of reaction interfaces near corners (?)

Further research (Simulation)

- Error estimates in 1D for non-equilibrium models in 2 phases
- Quantitative *a posteriori* error estimates for 2D semi-linear RD systems (+ their use in ALBERTA)
- numerical framework for $\epsilon \to 0$ and $\Phi^2 \to \infty$
- Stefan-Signorini conditions driving moving interfaces (1D)