Mathematical modelling of concrete:

Coupling flow and reaction chemistry in porous materials

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Outline

1. Introduction
   - What is concrete?
   - Concrete composition and chemistry
   - Motivation: Re-wetting experiments

2. Mathematical model
   - Physical set-up
   - Governing equations

3. Numerical simulations
   - Clogging simulation
   - Sensitivity study
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Why study concrete?

Concrete has a reputation as a “low tech” material, but it is actually very complex and worthy of study! Furthermore . . .

- It’s the most widely used construction material in the world. In 1997, 6.4B $m^3$ was produced – that’s 2.5 T per person!
- Of any material, only water has a higher consumption rate.
- It’s a climate change villain: the cement industry produces 5–10% of man-made CO$_2$ globally.
The words “cement” and “concrete” are frequently misused/confused.

**Cement:**
- Is a binding agent that hardens and holds other materials together.
- Ingredients: limestone, clay, gypsum, and other additives.

**Concrete:**
- Is a mixture of cement, aggregate (gravel or crushed stone), sand, and water.
- Concrete hardens after mixing with water through a process called hydration.
Concrete composition

- A typical concrete mix: cement (11%), gravel (41%), sand (26%), water (16%) and air voids (6%).
- This composition changes over time as the cement hydrates and concrete hardens.

Figure 4-26. Estimates of the relative volumes of cement compounds and products of hydration with increasing hydration (adapted from Tennis and Jennings 2000).
Note: These estimates are for a 0.50 water-cementitious materials ratio; decreasing the ratio will decrease the capillary porosity.
The primary (active) ingredients in Portland cement are:

- **Tricalcium silicate or “alite”**: $3\text{CaO} \cdot \text{SiO}_2$ (55%) \(\text{C}_3\text{S}\) (55%)
- **Dicalcium silicate or “belite”**: $2\text{CaO} \cdot \text{SiO}_2$ (18%) \(\text{C}_2\text{S}\) (18%)
- **Tricalcium aluminate**: $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ (10%) \(\text{C}_3\text{A}\) (10%)
- **Tetracalcium aluminoferrite**: $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ (8%) \(\text{C}_4\text{AF}\) (8%)

Water is the other main reactant: \(\text{H}_2\text{O}\) H

Main reaction products are **calcium silicate hydrate gel**: $3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O}$ \(\text{C}_3\text{S}_2\text{H}_3\) or simply \(\text{C-S-H}\)

and **calcium hydroxide**: \(\text{Ca(OH)}_2\) CH

**Simplify**: use standard cement chemistry notation

\[
\begin{align*}
C &= \text{CaO}, & S &= \text{SiO}_2, & H &= \text{H}_2\text{O}, & A &= \text{Al}_2\text{O}_3, & F &= \text{Fe}_2\text{O}_3
\end{align*}
\]
Main reactions for alite and belite:

\[ 2\text{C}_3\text{S} + 6\text{H} \xrightarrow{r_a} \text{C-S-H (aq)} + 3\text{CH} \]
\[ 2\text{C}_2\text{S} + 4\text{H} \xrightarrow{r_b} \text{C-S-H (aq)} + \text{CH} \]

**Note:** Alite reaction is much faster than belite: \( r_a \gg r_b \)

**Precipitation/dissolution:** gel forms from aqueous C-S-H

\[ \text{C-S-H (aq)} \xrightleftharpoons[k_{\text{prec}}]{k_{\text{diss}}} \text{C-S-H (gel)} \]
**Cement chemistry 3**

- **Initial hydration**: formation of crystalline “fingers” on silicate grains.
- **Setting**: over a period of hours, C-S-H gel matrix forms rapidly.
- **Clogging**: C-S-H gel causes porosity to decrease.
- **Hardening/curing**: hydration continues for days and even months.
Concrete structure

Hardened concrete has a complex, **multi-scale** porous structure with
gel pores (10–100 nm) $\ll$ capillary pores (10 $\mu$m) $\ll$ air voids (1 mm)
**Motivation: Re-wetting experiments**

Barrita (2002) studied re-wetting of hardened concrete with both isopropanol (non-reactive) and water (reactive) and observed . . .

**With isopropanol**

Wetting front obeys the usual $x = \alpha t^{1/2}$ for porous media flow.

**With water**

Wetting front stalls! Water behaves differently from isopropanol.
Hypothesis (from experimentalists):

Re-hydration of residual (unreacted) silicates leads to C-S-H gel formation that in turn clogs capillary pores.

Note:

- Initial hydration and setting phases have been modelled extensively, e.g. Bentz et al. (1994), Tzschichholz et al. (1995), Preece et al. (2001), etc.
- Hall et al. (1995) present experimental evidence that re-wetting leads to “anomalously low absorption rates.”
- However, re-wetting has not been modelled to date.
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Barrita, Bremner & Balcom (2003):

- A long, thin, cylindrical sample of dry concrete.
- Sides are sealed.
- Bottom is placed in a liquid reservoir.
- Wetting front moves upwards due to capillary action.
Main assumptions

1. Problem is one-dimensional (sample is long and thin).
2. Liquid transport obeys Darcy’s law (capillary pore scale only).
3. No temperature variations (reactions are slow).
4. Gravity is negligible (pores are small, low $Bo = \frac{\rho g L^2}{\gamma}$).
5. Consider only silicate reactions ($C_3S$ and $C_2S$ make up 70–80% of active ingredients).
6. Neglect individual ionic species.
7. Ignore chemical shrinkage.
Variables

Define the following dependent variables:

\[ \theta(x, t) = \text{liquid saturation} \]
\[ C_a(x, t) = C_3S \text{ (alite) concentration} \]
\[ C_b(x, t) = C_2S \text{ (belite) concentration} \]
\[ C_q(x, t) = \text{aqueous C-S-H concentration} \]
\[ C_g(x, t) = \text{solid C-S-H gel concentration} \]

An important supplementary variable is porosity:

\[ \varepsilon(x, t) = \varepsilon_o - \frac{C_g(x, t)}{\rho_g} \]
Conservation laws

Water:
\[
\frac{\partial \theta}{\partial t} + \frac{\partial}{\partial x} \left( -D(\theta, \varepsilon) \frac{\partial \theta}{\partial x} \right) = -R_\theta
\]

Darcy flux = \( u \)

Alite:
\[
\frac{\partial (\theta C_a)}{\partial t} + \frac{\partial (u C_a)}{\partial x} = \frac{\partial}{\partial x} \left( \theta D_a \frac{\partial C_a}{\partial x} \right) - R_a
\]

Belite:
\[
\frac{\partial (\theta C_b)}{\partial t} + \frac{\partial (u C_b)}{\partial x} = \frac{\partial}{\partial x} \left( \theta D_b \frac{\partial C_b}{\partial x} \right) - R_b
\]

Aqueous C-S-H:
\[
\frac{\partial (\theta C_q)}{\partial t} + \frac{\partial (u C_q)}{\partial x} = \frac{\partial}{\partial x} \left( \theta D_q \frac{\partial C_q}{\partial x} \right) + R_q
\]

C-S-H gel:
\[
\frac{\partial (\theta C_g)}{\partial t} = R_g
\]
**Reaction terms**

**Consumption of alite:**

\[ R_a = k_a C_a^{n_a} (\theta - \theta_{\text{min}})^+ \]

\[ = \min(\theta - \theta_{\text{min}}, 0) \]

(“shut-off”)

**Consumption of belite:**

\[ R_b = k_b C_b^{n_b} (\theta - \theta_{\text{min}})^+ \]

**Generation of C-S-H (aq + gel):**

(weighted by molar masses)

\[ R_{\text{csh}} = \frac{m_{\text{csh}}}{2} \left( \frac{R_a}{m_a} + \frac{R_b}{m_b} \right) \]

**Generation of water:**

\[ R_\theta = k_\theta R_{\text{csh}} \]

**Generation of C-S-H (aq):**

\[ R_q = R_{\text{csh}} - R_g \]

**Generation of C-S-H (gel):**

(precipitation and dissolution)

\[ R_g = (k_{\text{prec}} C_q - k_{\text{diss}} C_g) (\theta - \theta_{\text{min}})^+ \]
Water diffusion coefficient

\[ D(\theta, \varepsilon) = A e^{B\theta} \left( \frac{\varepsilon - \theta_{\text{min}}}{\varepsilon_0 - \theta_{\text{min}}} \right)^{19/6} \left( \frac{\varepsilon - \theta_{\text{min}}}{\varepsilon_0 - \theta_{\text{min}}} \right) \]

clogging

- Exponential dependence on \( \theta \) is fit to concrete experiments, with \( B \approx 6 \) and \( A \approx 0.003 \).
- Saturation is governed by a nearly degenerate diffusion equation with some interesting mathematical properties . . . later . . .
- The second factor represents clogging, and is commonly employed for biofilms in soil (Clement et al., 1996).
Typical values of a few of the most important parameters:

- Sample length: \( L = 10 \text{ cm} \).
- Diffusivity: \( B = 6 \) and \( A = 0.003 \).
- Narrow range of saturation: \( \theta_{\text{min}} = 0.04, \theta_{\text{max}} = \varepsilon_o = 0.067 \).
- Reaction exponents: \( n_a = 2.65, n_b = 3.10 \).
- Reaction rates: \( k_a = 22.2 \text{ d}^{-1}, k_b = 3.04 \text{ d}^{-1} \).
- Precipitation/dissolution rates: \( k_{\text{prec}} = 32.2 \text{ d}^{-1}, k_{\text{diss}} = 0 \).

**Refs:** Papadakis et al. (1989), Bentz (2006).
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Employ a method of lines approach with a second-order centered finite volume discretization in space.

Use $N = 100$ grid points in space, which yields a coupled nonlinear system of $5N$ ODEs in time.

Solve using Matlab’s stiff solver `ode15s`.

Requires less than 1 min. on a Mac PowerBook.
Clogging simulation

Plots of saturation over 28 days, at 10 equally-spaced time values:

Without reactions ($k_a = k_b = 0$)

With reactions

Standard nonlinear diffusive behaviour.

Stalled front.
Discrepancy between initial slopes for water/isopropanol data is likely due to variations in samples used.

Results are fit to water data using two parameters:
- Choose $A = 0.003 \text{ cm}^2/\text{day}$ to match wetting front speed.
- Scale reaction rates to match stalling location.
Porosity is smallest (i.e., C-S-H gel concentration is largest) just behind the stall location $x \approx 2$ cm.
Most of the alite (and belite) reacts behind the front.
Some reactions still occur ahead of the stalled front.
Results are relatively insensitive to variations in parameters such as dissolution rate ($k_{\text{diss}}$) and diffusivity ($D_a$, $D_b$, $D_q$):

(Chapwanya et al., J. Eng. Math., 2009)
Results much more sensitive to changes in reaction rates ($k_\alpha$, $k_\beta$):

(Chapwanya et al., J. Eng. Math., 2009)
Summary & Conclusions

- Developed a model for transport and reaction of water and silicates in hardened concrete.
- Calibration and comparison to a very detailed set of experiments.
- Numerical simulations support the hypothesis that hydration of residual silicates is responsible for anomalous water transport observed in re-wetting experiments.
- Sensitivity studies identify the most important physical parameters.
Other results: Exponential diffusion

Water only: \[
\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x} \left( D(\theta) \frac{\partial \theta}{\partial x} \right) \quad \text{with} \quad D(\theta) = Ae^{B\theta}
\]

- Compare to the more common power-law diffusivity: \(D(\theta) = a\theta^b\) (classical PME).

- Previous asymptotic results for exponential \(D\):
  - Babu (1976)
  - Parslow et al. (1988)
  - Parlange et al. (1992)

- Our matched asymptotics yield higher accuracy:
  - Budd & JMS (2010)
Future work

- Further experiments are necessary to confirm our hypothesis about hydration of residual silicates (work with Barrita).
- Incorporate transport and reaction kinetics of individual ionic species, similar to other models of initial hydration, carbonation (Meier et al., 2007), and chlorination (Papadakis et al., 1992).
- Derive analytical results on wetting front motion and stall location, à la Muntean & Böhm (2006).
- Numerical studies of the related phenomenon of self-desiccation and associated shrinkage effects.
- Applications: high-performance concrete, monument degradation and restoration, etc.
D. K. Babu.
Infiltration analysis and perturbation methods. 1. Absorption with exponential diffusivity.

P. Barrita.
Curing of high-performance concrete in hot dry climates studied using magnetic resonance imaging.

P. Barrita, T. W. Bremner, and B. J. Balcom.
Effects of curing temperature on moisture distribution, drying and water absorption in self-compacting concrete.
D. P. Bentz.
Influence of water-to-cement ratio on hydration kinetics: Simple models based on spatial considerations.

Cellular automaton simulations of cement hydration and microstructure development.

C. J. Budd and J. M. Stockie.
Asymptotic behaviour of wetting fronts in porous media with exponential moisture diffusivity.
A model for reactive porous transport during re-wetting of hardened concrete.  

T. P. Clement, B. S. Hooker, and R. S. Skeen.  
Macroscopic models for predicting changes in saturated porous media properties cause by microbial growth.  

Water anomaly in capillary liquid absorption by cement-based materials.  
S. A. Meier, M. A. Peter, A. Muntean, and M. Böhm.
Dynamics of the internal reaction layer arising during carbonation of concrete.

A. Muntean and M. Böhm.
Length scales in the concrete carbonation process and water barrier effect: A matched asymptotics approach.

Hydration and carbonation of pozzolanic cements.
References V

V. G. Papadakis, C. G. Vayenas, and M. N. Fardis.  
A reaction engineering approach to the problem of concrete carbonation.  

Extension of the Heaslet-Alksne technique to arbitrary soil water diffusivities.  

J. Parslow, D. Lockington, and J.-Y. Parlange.  
A new perturbation expansion for horizontal infiltration and sorptivity estimates.  

S. J. Preece, J. Billingham, and A. C. King.  
On the initial stages of cement hydration.  
F. Tzschichholz, H. J. Herrmann, and H. Zanni.  
A reaction-diffusion model for the hydration/setting of cement.  