

# Mathematical modelling of concrete:

## Coupling flow and reaction chemistry in porous materials

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Canadian Symposium on Fluid Dynamics  
CAIMS\*SCMAI 2010

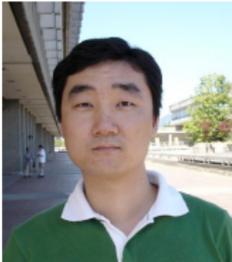
July 19, 2010

# Acknowledgments



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Funded by:



**NSERC**  
**CRSNG**



**MITACS**

# 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.



# Cement versus concrete?

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.



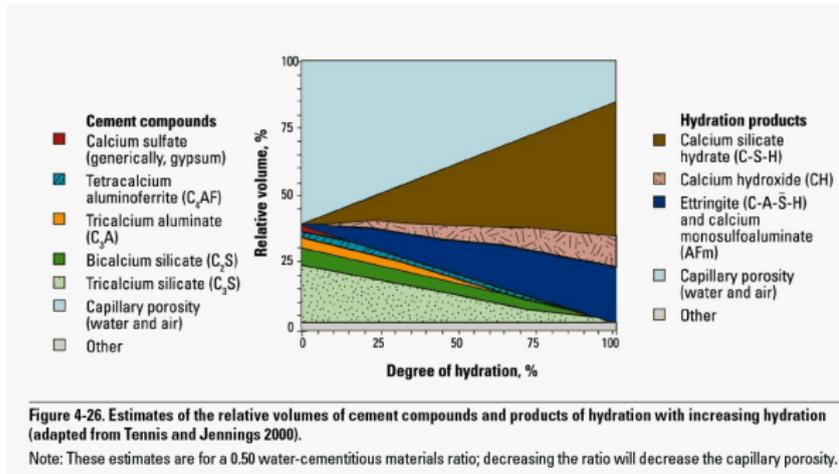
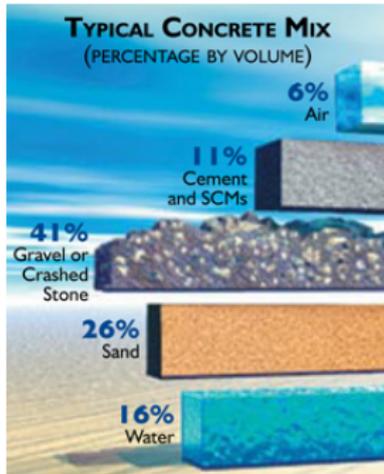
## Concrete:

- 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.

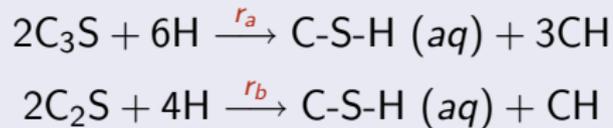


# Cement chemistry

- 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:
 
$$3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O} \text{ } \text{C}_3\text{S}_2\text{H}_3$$
 or simply **C-S-H**  
 and calcium hydroxide:  $\text{Ca}(\text{OH})_2$  **CH**
- **Simplify:** use standard cement chemistry notation
 
$$\text{C} = \text{CaO}, \quad \text{S} = \text{SiO}_2, \quad \text{H} = \text{H}_2\text{O}, \quad \text{A} = \text{Al}_2\text{O}_3, \quad \text{F} = \text{Fe}_2\text{O}_3$$

## Cement chemistry 2

Main reactions for alite and belite:



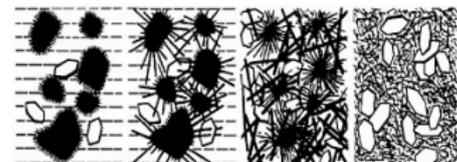
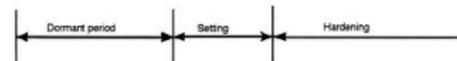
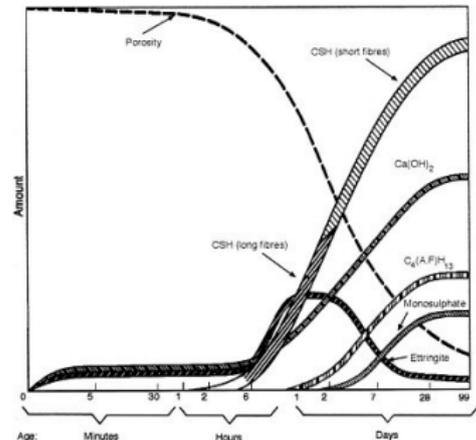
**Note:** Alite reaction is much faster than belite:  $r_a \gg r_b$

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



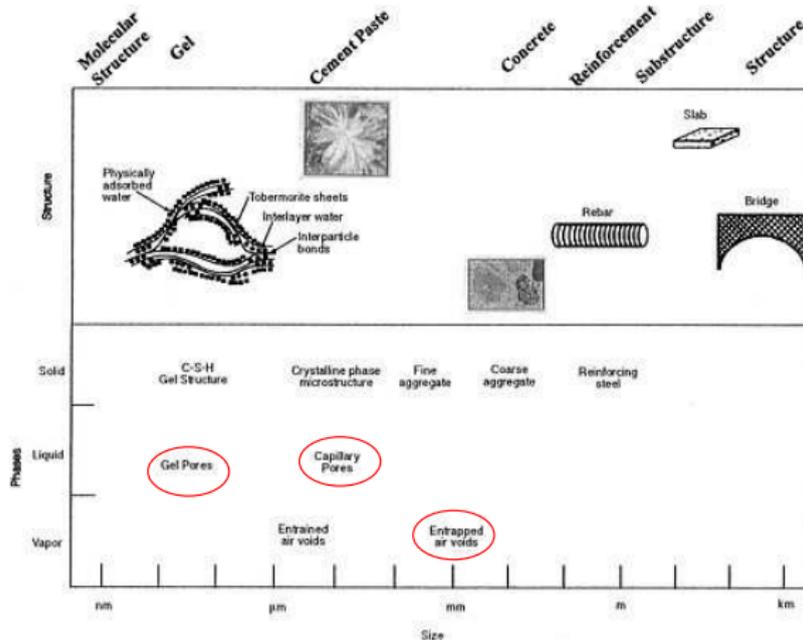
# Cement chemistry 3

- **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

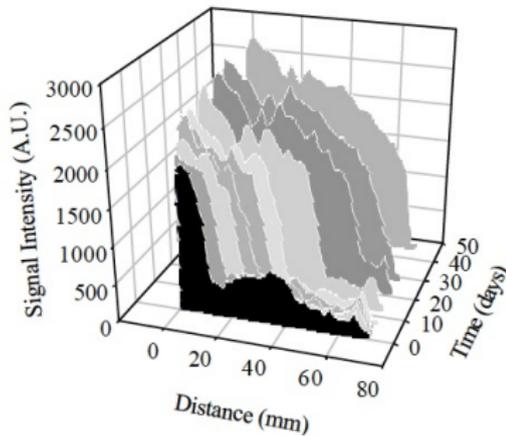
Hardened concrete has a complex, multi-scale porous structure with gel pores (10–100 nm)  $\ll$  capillary pores (10  $\mu\text{m}$ )  $\ll$  air voids (1 mm)



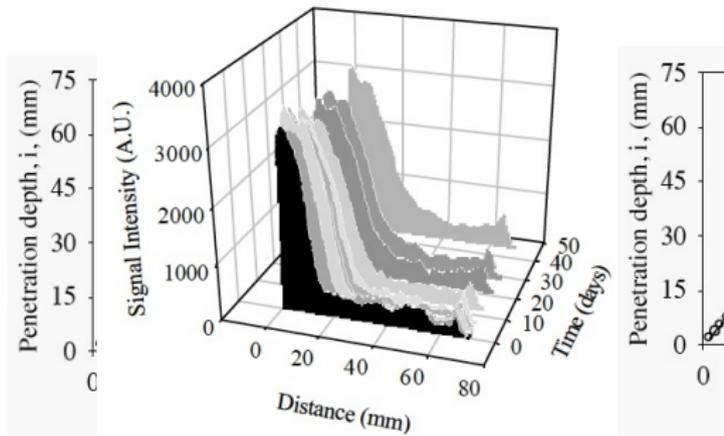
# Motivation: Re-wetting experiments

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

With isopropanol



With water



Wetting front obeys the usual

# Main hypothesis

## 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.

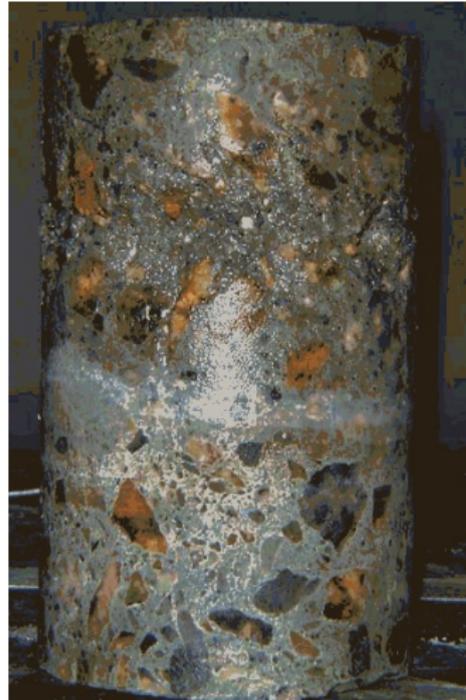
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# Barrita's re-wetting experiment

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



## 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:

$\theta(x, t)$  = liquid saturation

$C_a(x, t)$  =  $C_3S$  (**a**lite) concentration

$C_b(x, t)$  =  $C_2S$  (**b**elite) concentration

$C_q(x, t)$  = **a**queous C-S-H concentration

$C_g(x, t)$  = solid C-S-H **g**el concentration

An important supplementary variable is **porosity**:

$$\varepsilon(x, t) = \varepsilon_o - \frac{C_g(x, t)}{\rho_g}$$

## Conservation laws

$$\text{Water:} \quad \frac{\partial \theta}{\partial t} + \frac{\partial}{\partial x} \left( \underbrace{-D(\theta, \varepsilon) \frac{\partial \theta}{\partial x}}_{\text{Darcy flux} = u} \right) = -R_\theta$$

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

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

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

$$\text{C-S-H gel:} \quad \frac{\partial(\theta C_g)}{\partial t} = R_g$$

# Reaction terms

Consumption of alite:

$$R_a = k_a C_a^{n_a} \underbrace{(\theta - \theta_{\min})_+}_{= \min(\theta - \theta_{\min}, 0)} \\ \text{("shut-off")}$$

Consumption of belite:

$$R_b = k_b C_b^{n_b} (\theta - \theta_{\min})_+$$

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):

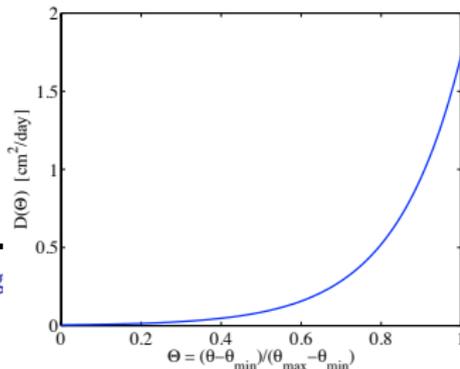
$$R_q = R_{\text{csh}} - R_g$$

Generation of C-S-H (gel):  
(precipitation and dissolution)

$$R_g = (k_{\text{prec}} C_q - k_{\text{diss}} C_g) (\theta - \theta_{\min})_+$$

# Water diffusion coefficient

$$D(\theta, \varepsilon) = Ae^{B\theta} \left( \frac{\varepsilon - \theta_{\min}}{\varepsilon_o - \theta_{\min}} \right)^{19/6} \underbrace{\left( \frac{\varepsilon - \theta_{\min}}{\varepsilon_o - \theta_{\min}} \right)}_{\text{clogging}} \frac{D(\theta) \text{ [cm}^2\text{/day]}}{D(\theta)}$$



- 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).

# Parameter values

Typical values of a few of the most important parameters:

- Sample length:  $L = 10$  cm.
- Diffusivity:  $B = 6$  and  $A = 0.003$ .
- Narrow range of saturation:  $\theta_{\min} = 0.04$ ,  $\theta_{\max} = \varepsilon_o = 0.067$ .
- 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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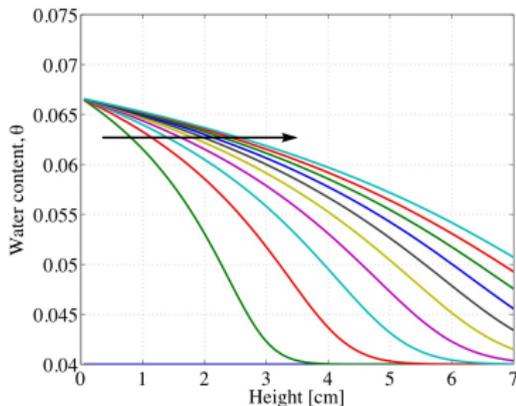
## Solution algorithm

- 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

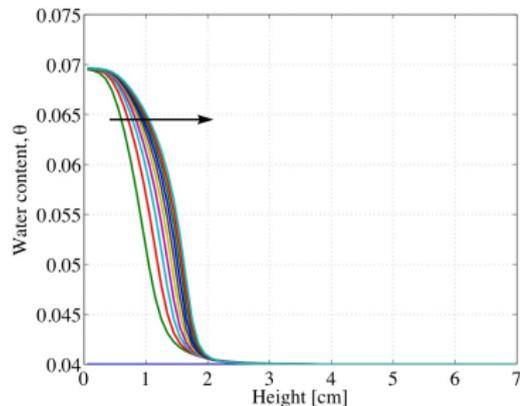
Plots of saturation over 28 days, at 10 equally-spaced time values:

Without reactions ( $k_a = k_b = 0$ )



Standard nonlinear diffusive behaviour.

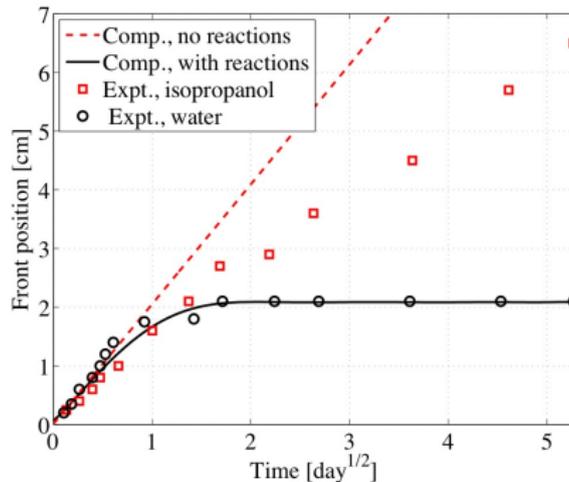
With reactions



Stalled front.

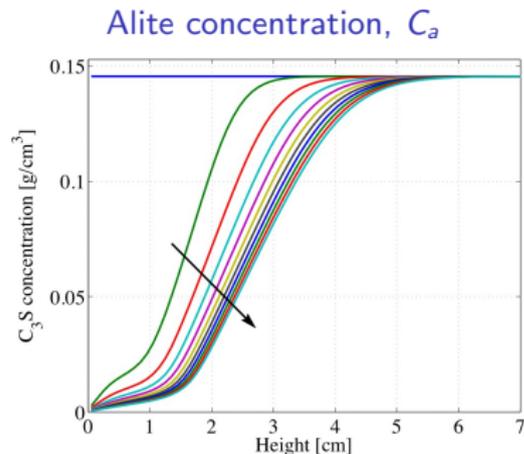
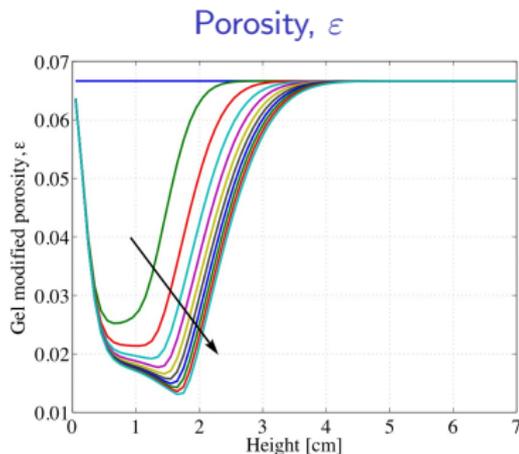
## Clogging simulation 2

- 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.



# Clogging simulation 3

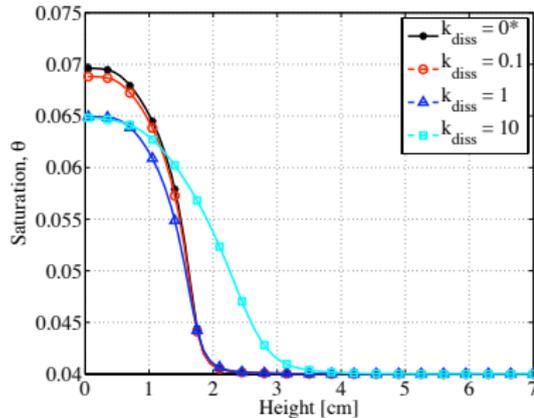
- Porosity is smallest (i.e., C-S-H gel concentration is largest) just behind the stall location  $x \approx 2$  cm.
- Most of the alite (and belite) reacts behind the front.
- Some reactions still occur ahead of the stalled front.



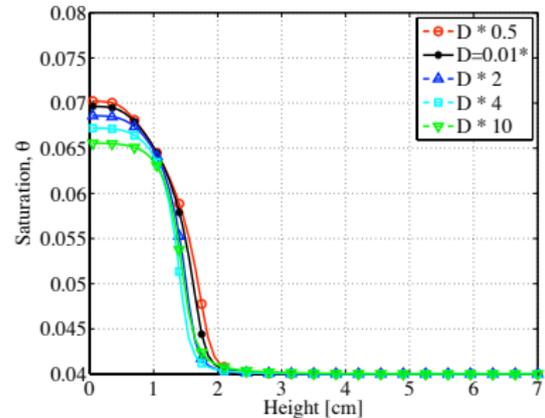
# Sensitivity study

Results are relatively insensitive to variations in parameters such as dissolution rate ( $k_{\text{diss}}$ ) and diffusivity ( $D_a, D_b, D_q$ ):

Final saturation



Final saturation

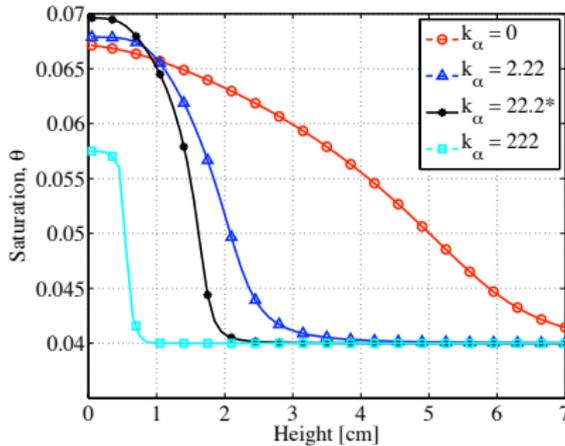


(Chapwanya et al., J. Eng. Math., 2009)

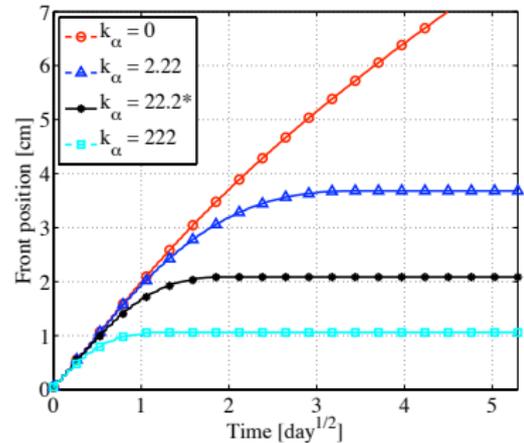
# Sensitivity study 2

Results much more sensitive to changes in reaction rates ( $k_\alpha$ ,  $k_\beta$ ):

Final saturation



Wetting front position



(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

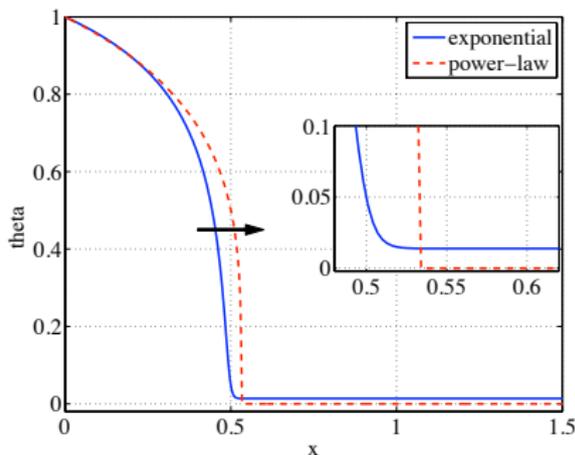
Water only:  $\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x} \left( D(\theta) \frac{\partial \theta}{\partial x} \right)$  with  $D(\theta) = Ae^{B\theta}$

- 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)



$D(\theta) = a\theta^b$  ( $b > 1$ ): degenerate

$D(\theta) = Ae^{B\theta}$ : nearly degenerate

## 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.

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