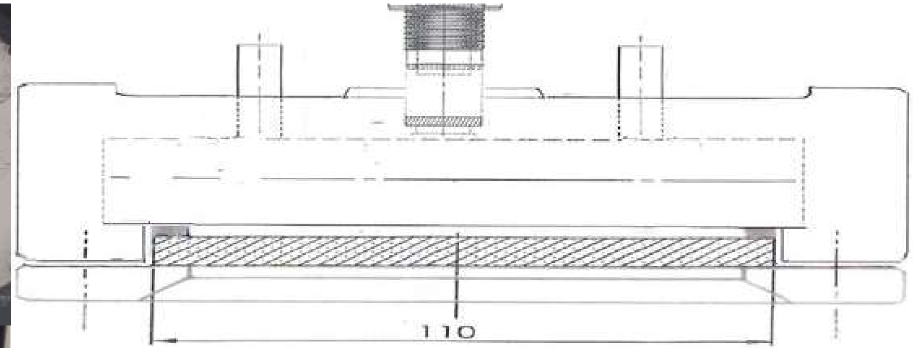
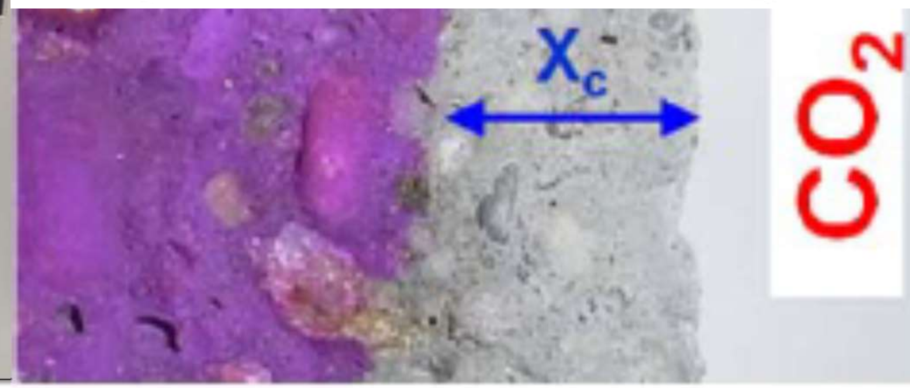




Carbonation of Cement based materials - a benchmark for reactive transport models ?

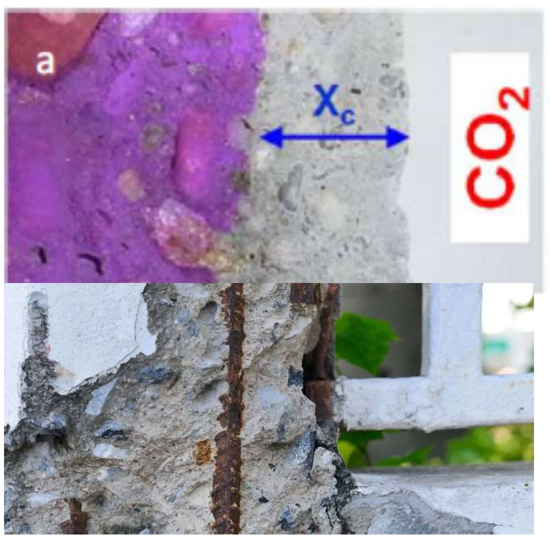
B. Huet, R. Barbarulo, M. Boumaaza, Ga. Pham, Q.H. Vu

LafargeHolcim

Context - Concrete Carbonation, to what end ?

Durability

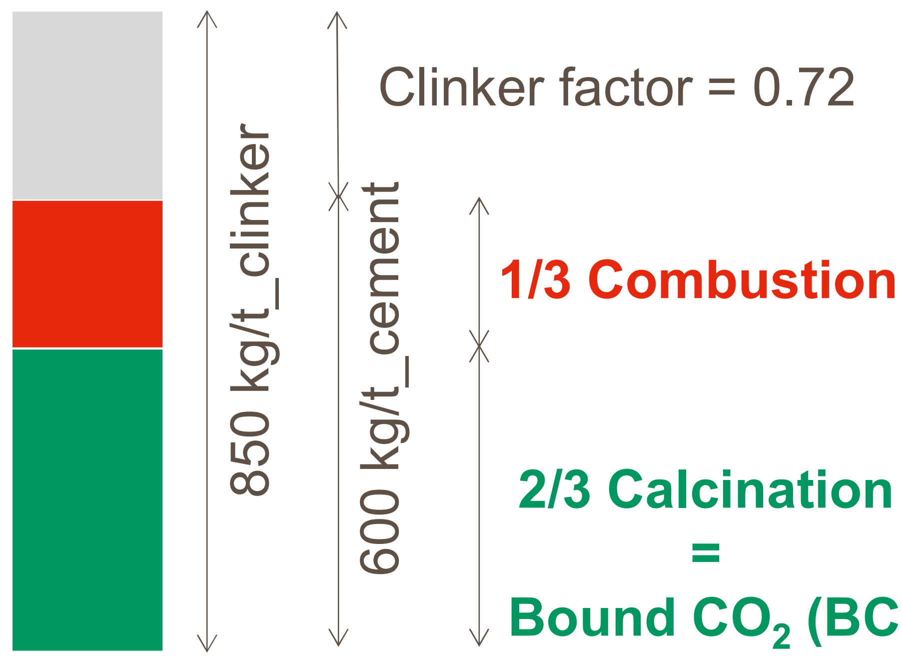
- Carbonation and corrosion



- Xc carbonation depth (pH drop)

Sustainability

- CO_2 emissions



$$\boldsymbol{X_c} \overset{?}{=} \sqrt{\frac{\boldsymbol{D_g}\ [CO_2]}{\rho_{cem}\ \boldsymbol{BC}}}$$

Context – carbonation modeling

An urgent need for concrete carbonation model

- **Standardization**
  - Concrete CEN/TC 104 "Exposure Resistance Classes (RC)" == > EN 12390 - XX
  - Structural analysis CEN/TC 250/SC 2/WG 1 TG10 "Durability" == > EUROCODE
  - Environmental Product Declaration CEN/TC 229-CF == > EN 16757- includes a model !)
- **Technical committees**
  - FIB COM8 Durability:
    - 8.8 Limit States, 8.9WG1 Initiation (Gehlen), 8.9WG2 Propagation (Andrade)
  - RILEM TC CCC WG3 "Carbonation modeling"
  - PerfDuB/Modevie, "Performance Assessment of Durability of Concrete"
- **Academia**
  - Scopus: "Concrete" AND "carbonat*" AND "model*" == > N=95 over last 5 y. !!!

(TITLE-ABS-KEY (concrete) AND TITLE-ABS-KEY (carbonat*) AND TITLE (model*)) AND DOCTYPE (ar OR r

Today – Open Challenges for models

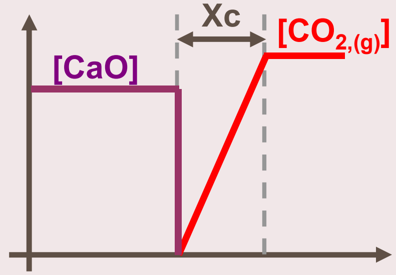
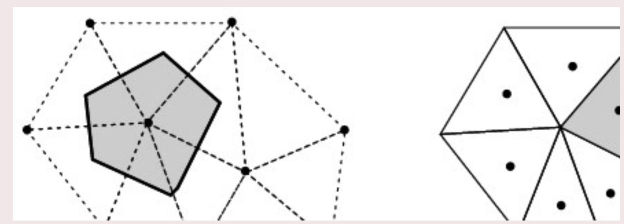
Specifications of Engineering models of atmospheric carbonation

- Match real behavior
  - Real mix design, different Geometries
  - Real execution: 1- 3 d. curing
  - Real Climate: Sun, Wind, Rain
- Community Acceptance:
  - Simple and transferable Principles
  - Rely on facts and measured properties
- General purpose: same principles/models at every stage of product life cycle
  - Carbonation for **corrosion** initiation
  - Carbonation for Recycled Concrete Aggregate (**RCA**)

Need to for validated model beyond analytical srt(time)

Today - a large range of modeling strategies

Example from both end of the spectrum: different characteristics

Property	"Engineering"	Reactive Transport
Principles	Front tracking	Spatial discretization
Discretization		
Go. Equ.	ODE: $[CaO].\dot{X}_c = \left(D_{e,g}.\left[CO_{2,(g)}\right]\right)/X_c$	PDE: $\frac{\partial \phi S_l \mathcal{C}_i^l}{\partial t} = -\nabla\cdot(\mathcal{C}_i^l q_l - D_l^e \nabla \mathcal{C}_i^l)$
Geometry	1D	3D
Linearity ?	Linear	Non-Linear
Resolution	Analytical	Numerical , e.g. with Finite volume
Chemistry	Not accounted for	Full Geochemistry
Calibration	$1/\boldsymbol{R_N} = \left(D_{e,g} * \left[CO_{2,(g)}\right]\right)/[CaO]$	Measured properties & Profiles

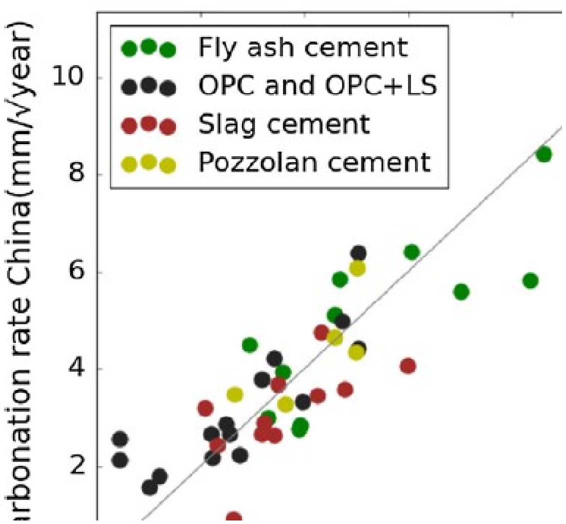
Today – some current calibration limits – curing and weather functions

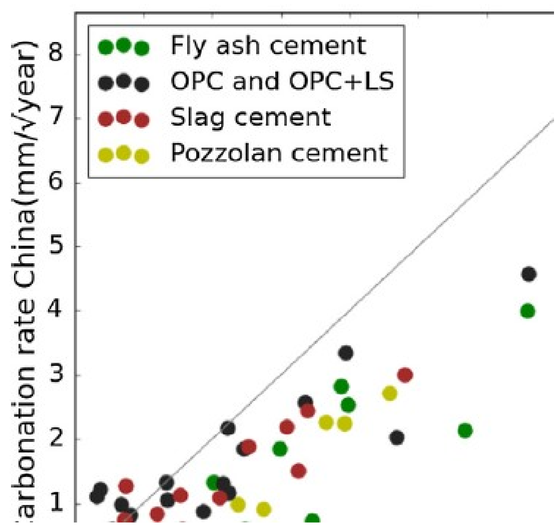
Weather – sheltered vs unsheltered [Vu 2019]

- Two different climates:

City	<RH>	<T>	<N_rain>
Austin, USA	~65	~20	~90
Changsha, China	~70	~20	~150

Sheltered = no Rain





UnSheltered = Rain

Key difference: Number of rainy day per year

2019, Vu et al. “Impact of different climates on the resistance of concrete to natural carbonation”

Future – alternative carbonation model strategies

A different choice of properties and conditions

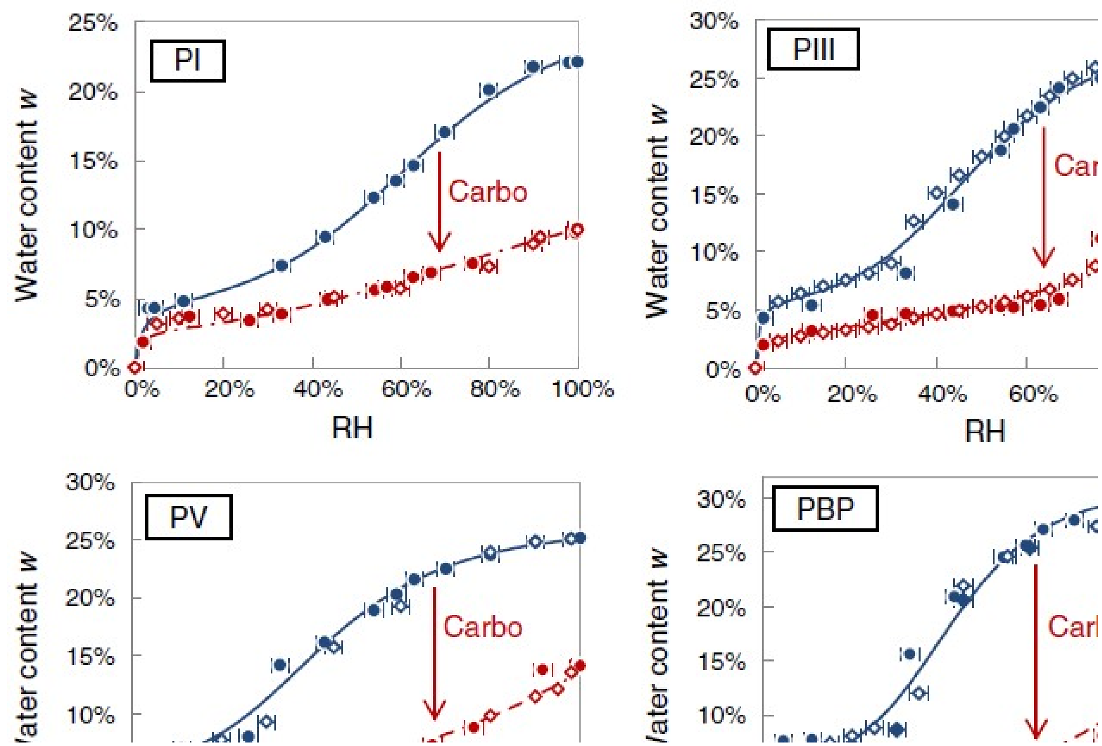
- Key properties, which depend on Degree of Carbonation (DoC)
  1. **Isothermal Water sorption**
  2. **Permeability for Drying/Wetting**
  3. **Gas diffusivity**
  4. **Carbonation reaction rate**
- To analyze:
  - Relevant **length and time scales** at play
  - **Carbonation profile**
- And predict
  - pH drop, i.e. durability !
  - And CO_2 uptake, i.e. sustainability !

Do we know these 4 main properties ?

Results (1) – Water sorption

Data before/after Carbonation (Auroy et al. CCR 2015)

- 4 different pastes (W/C=0.4)
  - PI : CEM I
  - PIII = CEM III
  - PV = CEM V
  - PBP= low pH



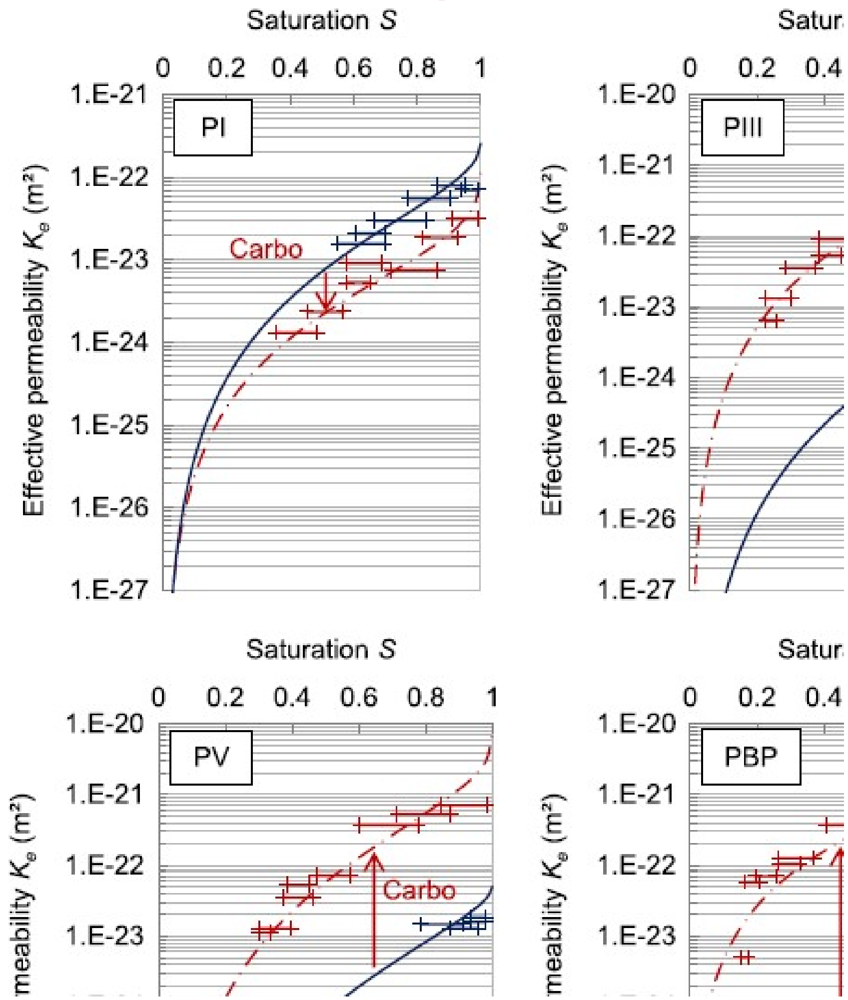
Significant change of sorption behavior with carbonation

Results (2) – Relative permeability from Drying

Data before/after Carbonation (Auroy et al. CCR 2015)

- 4 different pastes (W/C=0.4)
  - PI : CEM I
  - PIII = CEM III
  - PV = CEM V
  - PBP= low pH
- Inverse analysis of drying experiments

$$\varnothing\left(\frac{\partial S}{\partial P}\right)\frac{\partial P}{\partial t} = div\left[\frac{K_e}{\eta}\underline{grad}(P)\right] - .$$

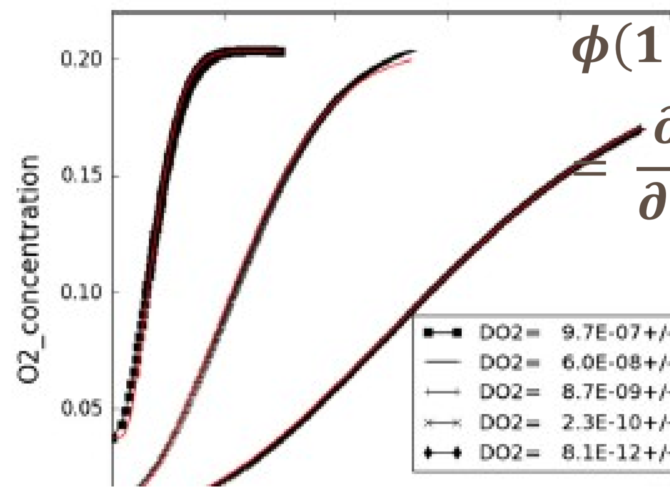


Permeability change by 2 orders of magnitude upon carbonation

Results (3) - Gas diffusivity – method principles

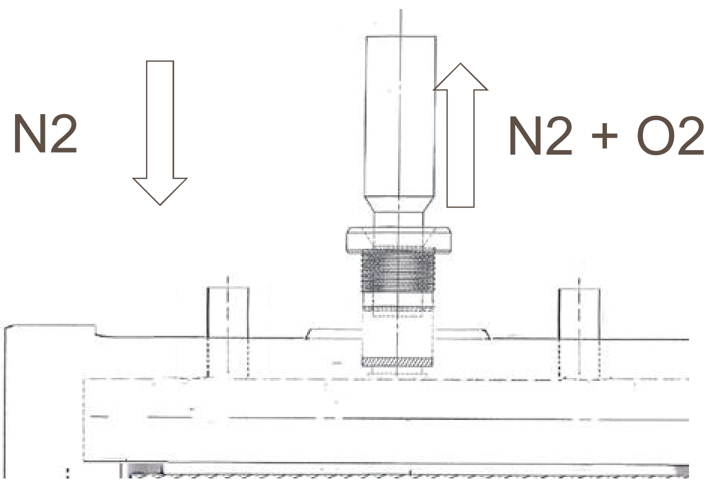
A – Equilibration in RH Chamber

C – Fitted O_2 accumulation

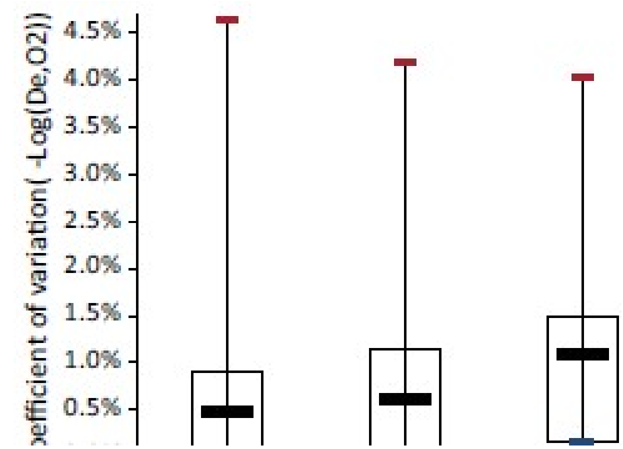


$$\phi(1-S_l)\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D_{e,O_2}\frac{\partial C}{\partial x}\right)$$

B - Diffusion Cell



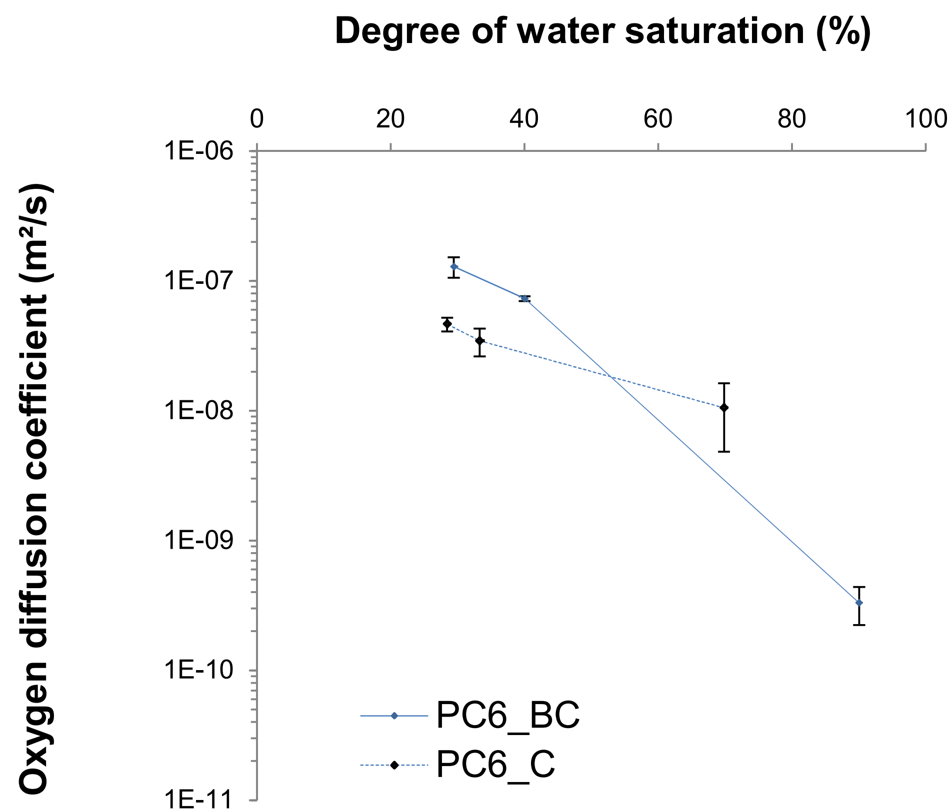
D – Results - Reproducibility



Results (3) – Gas diffusivity - Results

Role of RH and carbonation

- OPC paste (W/C 0.6)
- w/wo carbonation
  - Carbonated at 1% (DoC ~70%)
  - Along desorption
- Water porosity:
  - Before carbonation 50%
  - After carbonation: 37%



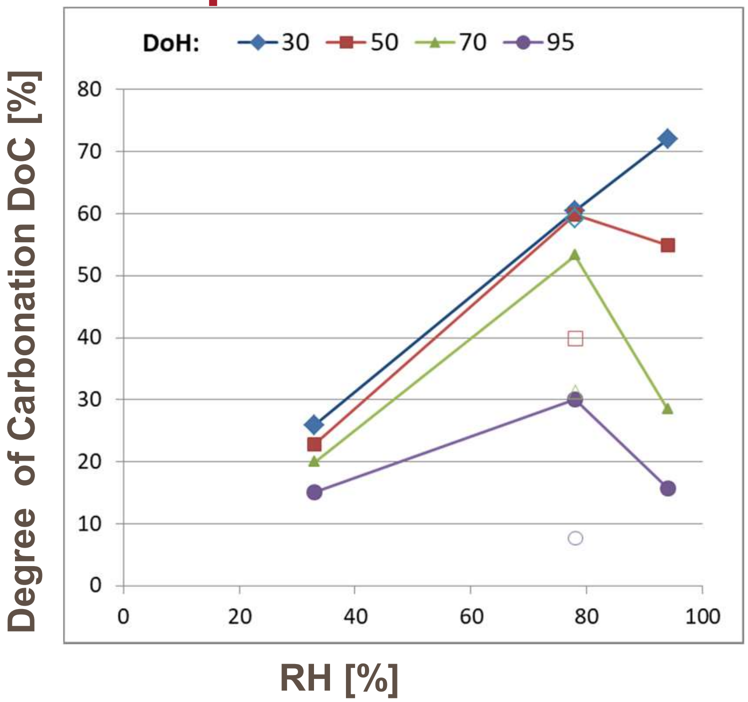
Both RH and DoC influence on Dg

Boumaaza ICCC 2019

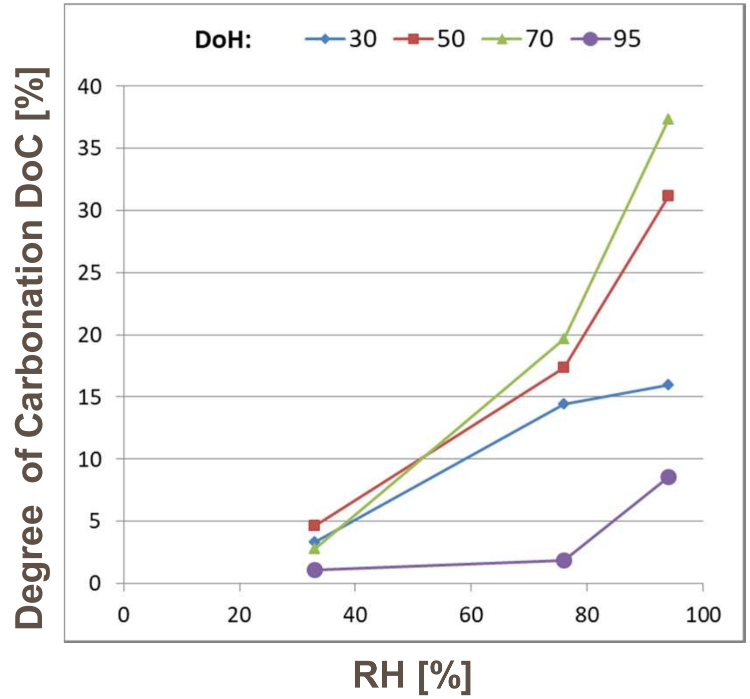
Results (1) – CO2 binding rate on C3S

Huet et al. ICCC 2019

1 – atmospheric carbonation



2 – accelerated carbonation



- Highest rate: **1e-6 [g_CO2/g_cement/s]**
- **Bell Shape Curve**
- No local maximum : monotonic increase

Non-linearity of carbonation rates with RH and DoC

Results (5) – relevant length and time scales analysis

Width of reaction zone – analytical calculation

- **Damköhler number**
  - Comparison of time scale in REV [kg_CO2/m3/s]
  - Reaction k_{CO2} [g_CO2/g_cement/s]
  - Effective Gas Diffusion De,g [m^2/s]

$$\rho_{cem}.k_{CO2} \overset{?}{<>} D_{e,g}.\frac{c_{CO2}}{L^2}$$

Huet et al. ICCC 2019

- Length scale for atmospheric carbonation **[m]**
  - CO_2 : 400 ppm
  - **From 50 µm** to 1.5 cm

k_{CO2} \ $D_{e,g}$	1.00E-06	1.00E-09
1.00E-06	1.55E-03	**4.90E-05**
1.00E-08	1.55E-02	4.90E-04

- Length scale for accelerated carbonation **[m]**
  - CO_2 : 3 %
  - From 400 µm **to 13 cm** !

k_{CO2} \ $D_{e,g}$	1.00E-06	1.00E-09
1.00E-06	1.34E-02	4.24E-04
1.00E-08	**1.34E-01**	4.24E-03

Length scale comparable to structure length scale [cm]
== > rate to be integrated in predictive models

Results(6) - Calculation of Carbonation profile

A simplified approach

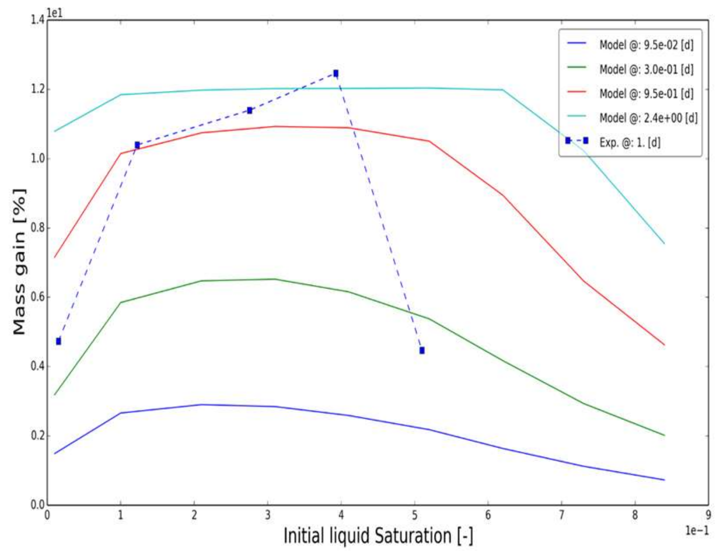
- Strategy = 1st order mechanisms
- general purpose PDE Solver = Fipy
- Data: CO_2 uptake on 4*4*16 samples (accelerated carbonation)

$$S_{cr}\frac{\partial C_{H_2O}}{\partial t} + \bar{\nabla}\left(\bar{J}_{H_2O}\right) = Q_{H_20}$$

$$S_{cr}\frac{\partial C_{CO_2}}{\partial t} + \bar{\nabla}\left(\bar{J}_{CO_2}\right) = Q_{CO_2}$$

$$S_{cr}\frac{\partial C_{CaO}}{\partial t} = 0$$

$$S_{cr}\frac{\partial C_{SiO_2}}{\partial t} = 0$$



Huet et al. Unpublished

Conclusion - benchmark proposal on carbonation

From experimental data to advanced reactive transport model – a proposed validation loop for concrete carbonation

1. Measured properties
   - Calibration of Constitutive laws: gas diffusion, rate, permeability(suction), sorption
2. Space/Time evolution:
   - Measured Carbonation profiles
   - Simplified model based on all purpose mixed PDE/ODE/NLAE solver (FiPy, others?)
3. Full Reactive transport calculation for Rock/Water/Gas interactions
   - Solving simplified Test problem with full models