Reactive transport modeling of coupled concrete carbonation and drying

FROM RESEARCH TO INDUSTRY

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ConCarb2019
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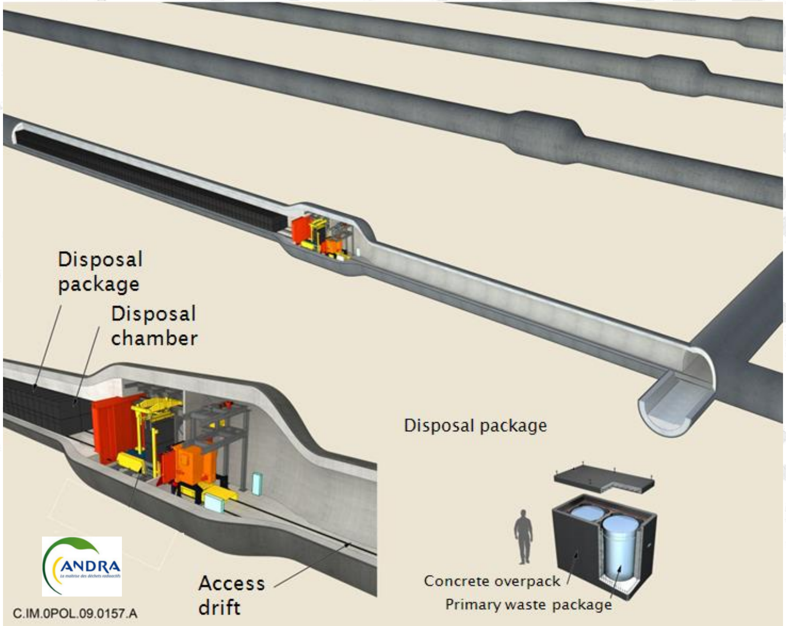
OUTLINE PLAN

- **Context of the study**
- **Phenomenology and modeling parameters**
- **Modeling accelerated concrete carbonation experiments**
- **A benchmark exercice for atmospheric concrete carbonation**
- **Conclusion and perspectives**

Deep geological storage of Intermediate Long Lived Waste (ILLW) ILLW cells, shafts (and seals) - ILLW disposal overpack

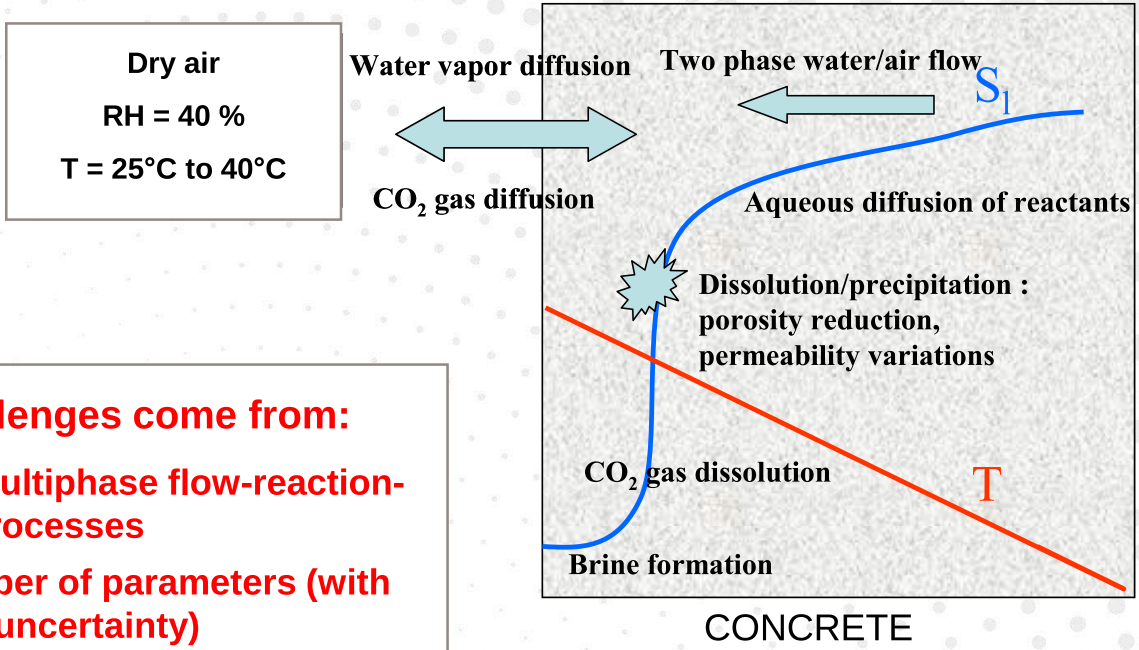
Atmospheric carbonation of concrete overpack during the operating period for :

- Bituminized waste
- Compacted metallic waste
- Organic waste



Phenomenology and modeling parameters

DRYING AND CARBONATION PROCESSES OF ILLW OVERPACK



Dry air

RH = 40 %

T = 25°C to 40°C

Water vapor diffusion

CO_2 gas diffusion

Two phase water/air flow

Aqueous diffusion of reactants

Dissolution/precipitation : porosity reduction, permeability variations

CO_2 gas dissolution

Brine formation

CONCRETE

Major challenges come from:

- **coupled multiphase flow-reaction-transport processes**
- **large number of parameters (with associated uncertainty)**

PHENOMENOLOGY: CAPILLARY FLOW

- ✓ Flow law (generalized Darcy law):

$$F_\beta = -k \frac{k_{r\beta}\rho_\beta}{\mu_\beta}(\vec{\nabla} P_\beta - \rho_\beta \vec{g})$$

- ✓ Lowering of the dew point due to capillary effects (Kelvin equation in EOS4):

$$P_{cap}(h_r) = -\rho_w \frac{RT}{M_w} \ln(h_r(S_l))$$

- ✓ Water relative permeability (Van Genuchten):

$$k_{rl}(S_r) = \sqrt{S_r}\left[1-\left(1-S_r^{\frac{1}{m}}\right)^m\right]^2 \qquad S_r = \frac{(S_l - S_{lr})}{(S_{ls} - S_{lr})}$$

- ✓ Gas relative permeability (Corey):

$$k_{rg} = \left(1-\hat{S}\right)^2\left(1-\hat{S}^2\right) \qquad \hat{S} = \frac{(S_l - S_{lr})}{(1 - S_{lr} - S_{gr})}$$

- ✓ Klinkenberg effect (gas flow at low pressure):

$$k_g = k_{\text{int}}\left(1 - \frac{\Gamma}{p}\right)k_{rg}$$

PHENOMENOLOGY: DIFFUSION

- ✓ Gaseous diffusion: $d_{0,i,\beta}(P,T) = d_{0,i,\beta}(P_0,T_0)\dfrac{P_0}{P}\left[\dfrac{T+273{,}15}{273{,}15}\right]^{\theta}$
- ✓ CO$_2$ and other gases: $d_{0,i,\beta} = \dfrac{RT}{3\sqrt{2}\pi PNd^2}\sqrt{\dfrac{8RT}{\pi M}}$
- ✓ Aqueous diffusion: $d_{0,i,\beta} = d_{H_2O,298{,}15K}\exp\left[\dfrac{E_a}{R}\left(\dfrac{1}{298{,}15}-\dfrac{1}{T}\right)\right]$
- ✓ Effective diffusion : $D_{i,\beta} = d_{0,i,\beta}\,\omega\,\tau_0\tau_\beta$
- ✓ Tortuosity (Millington-Quirk): $\tau_0\tau_\beta = \omega^a S_\beta^b$

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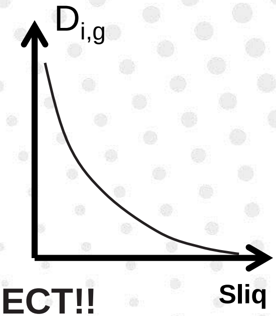
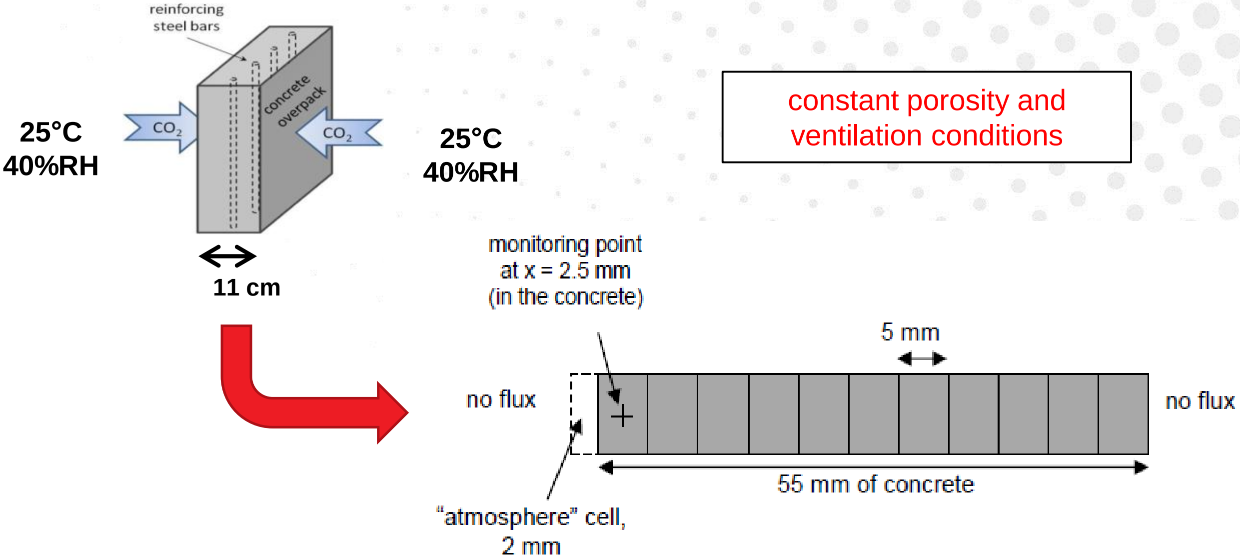


1st MAJOR COUPLING EFFECT!!

SIMULATIONS CONFIGURATION

- ✓ 1D half section overpack wall (section = 11 cm)
- ✓ Carbonation on both sides
- ✓ Ventilation air at 25°C and 40% relative humidity
- ✓ Initial liquid water saturation assumed to be 0.8



constant porosity and ventilation conditions

DRYING PHENOMENON : PARAMETERS VALUES

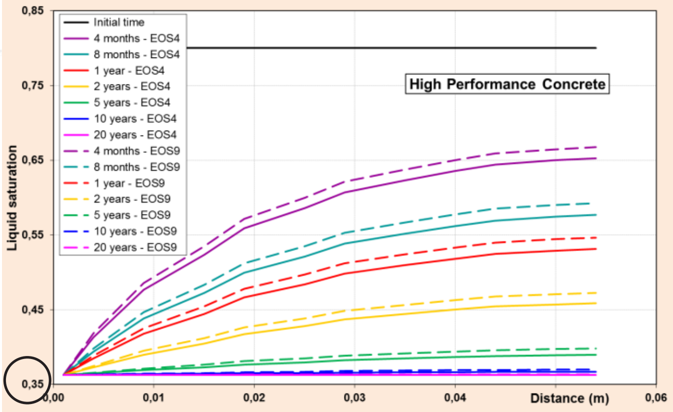
✓ different properties for concrete materials:
- High Performance Concrete (HPC)
- Intermediate Performance Concrete (IPC)
- Low Performance Concrete (LPC)

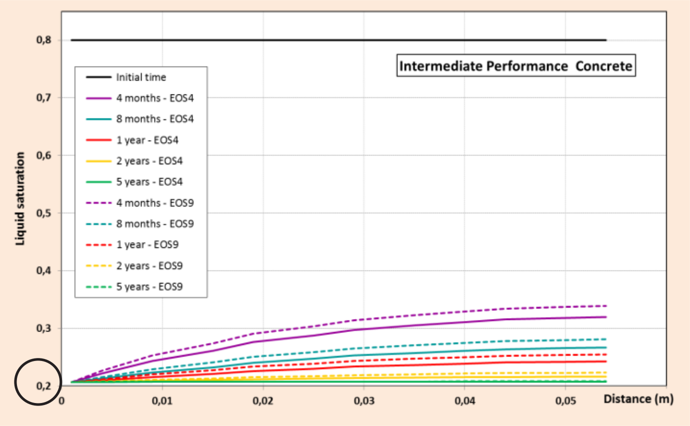
	HPC	IPC	LPC
Porosity	0.08	0.12	0.16
Intrinsic permeability to liquid (m²)	1e-21	1e-19	1e-17
Intrinsic permeability to gas (m²)	1e-19	1e-17	1e-15
Relative permeability m – Slr – Sls – Sgr	0.481 – 0.0 – 1.0 – 0.0	0.424 – 0.0 – 1.0 – 0.0	0.367 – 0.0 – 1.0 – 0.0
Capillarity pressure m – P_0 (MPa) – Pmax (MPa)	0.481 – 45 - 1500	0.424 – 15 - 1500	0.367 – 5 - 1500
Molecular diffusion coefficient gaseous phase (m²/s) water	2.4e-05		
Molecular diffusion coefficient gaseous phase (m²/s) CO_2	1.6e-05		
Molecular diffusion coefficient in aqueous phase (m²/s)	1.9e-09		
Millington-Quirk a parameter	2		
Millington-Quirk b parameter	4.2		
Klinkenberg parameter (MPa)	0.45		

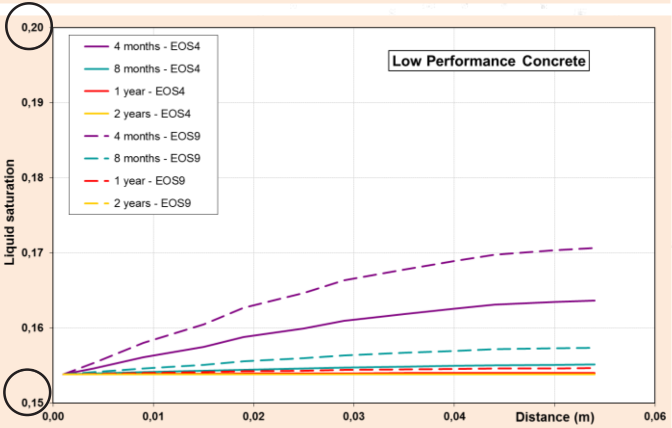
HPC chosen for the benchmarking exercise

DRYING RESULTS

- ✓ using Toughreact code in EOS9 mode (Richards) and EOS4 mode (full multiphase)







- ✓ Drying process slows down when transport characteristics of concrete are enhanced.
- ✓ Drying with Richards' equation (EOS9 without gaseous diffusion) is slightly slower than with full multiphase model (EOS4).

CHEMICAL PARAMETERS SIMULATING CEM V CONCRETE

✓ Primary phases

Phase	Volume %
Calcite	72.12
Portlandite	5.73
CSH 1.6	13.76
Monocarboaluminate	2.26
Ettringite	3.60
Hydrotalcite	0.39
Hydrogarnet-Fe (C3FH6)	2.05

✓ Secondary phases

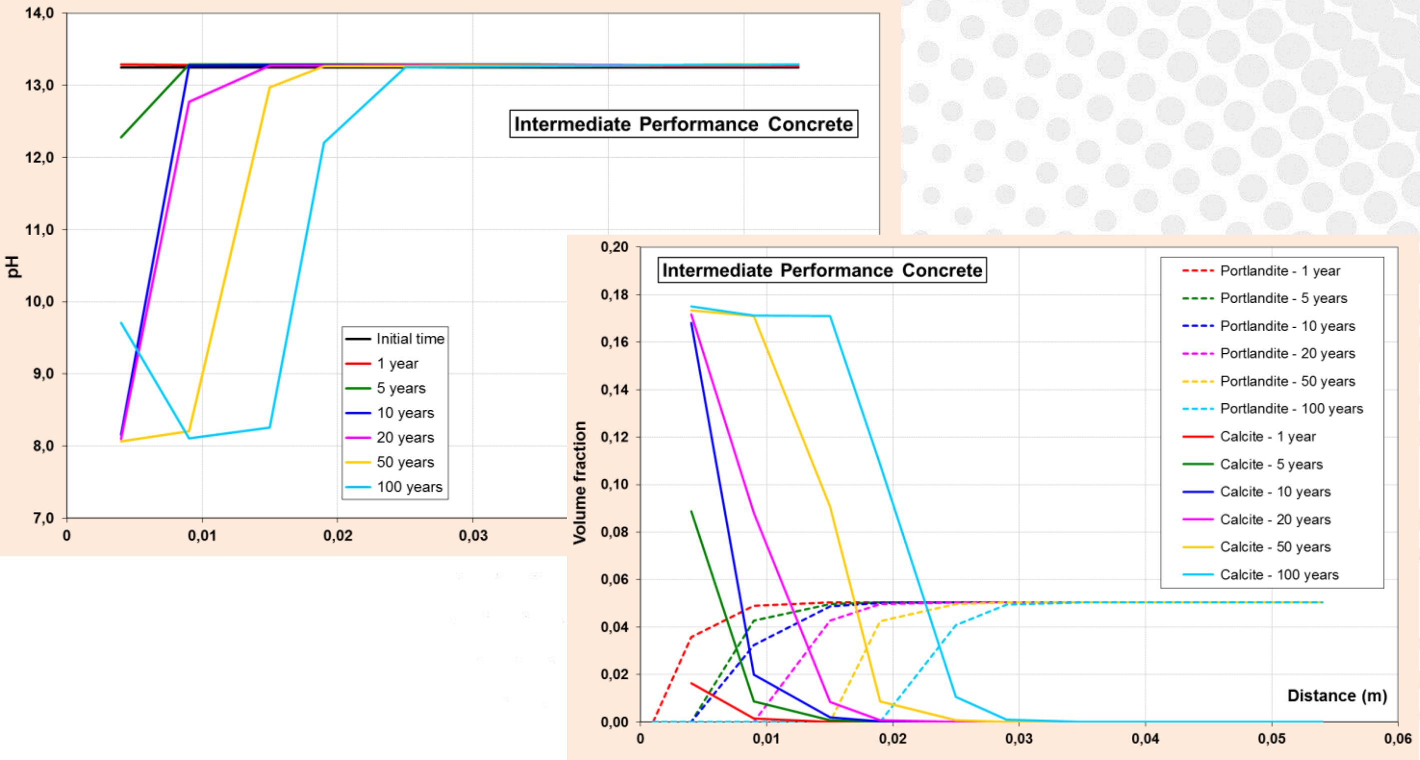
Phase type	Phases
Oxides	Magnetite, Amorphous silica
Hydroxides	Brucite, Gibbsite, $Fe(OH)_3$
Sheet silicates	Sepiolite
Other silicates	CSH 1.2, CSH 0.8, Straetlingite, Katoite_Si
Sulfates, chlorides, other salts	Gypsum, Anhydrite, Burkeite, Syngenite, Glaserite, Arcanite, Glauberite, Polyhalite
Carbonates	Calcite, Nahcolite
Other	Hydrotalcite-CO_3, Ettringite, Dawsonite

✓ Kinetics of dissolution / precipitation

$$r_n = \pm k_n A_n \left|1-\Omega_n^{\theta}\right|^{\eta}$$

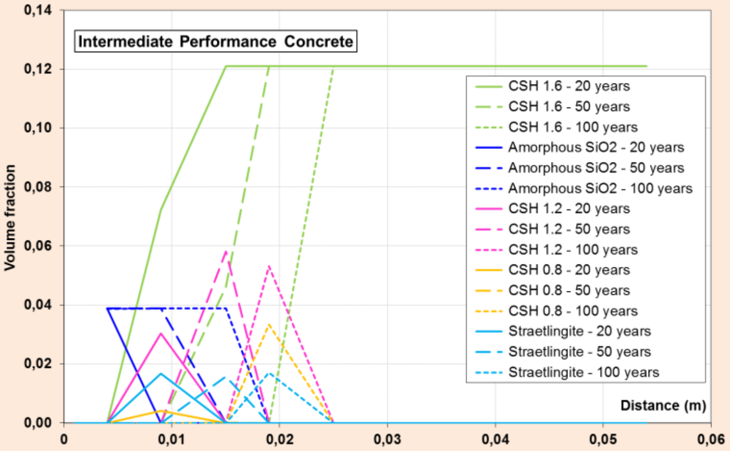
$$k_n(T) = k_{298,15} \exp\left[\frac{-E_a}{R}\left(\frac{1}{T}-\frac{1}{298,15}\right)\right]$$

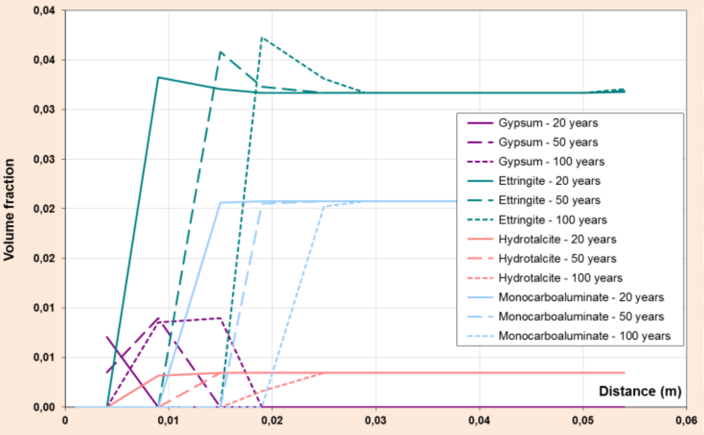
CARBONATION RESULTS



- ✓ pH decrease, portlandite dissolution and calcite precipitation over a thickness of about 2 cm after 100 years (1 cm for HPC, 4 cm for LPC)

CARBONATION RESULTS



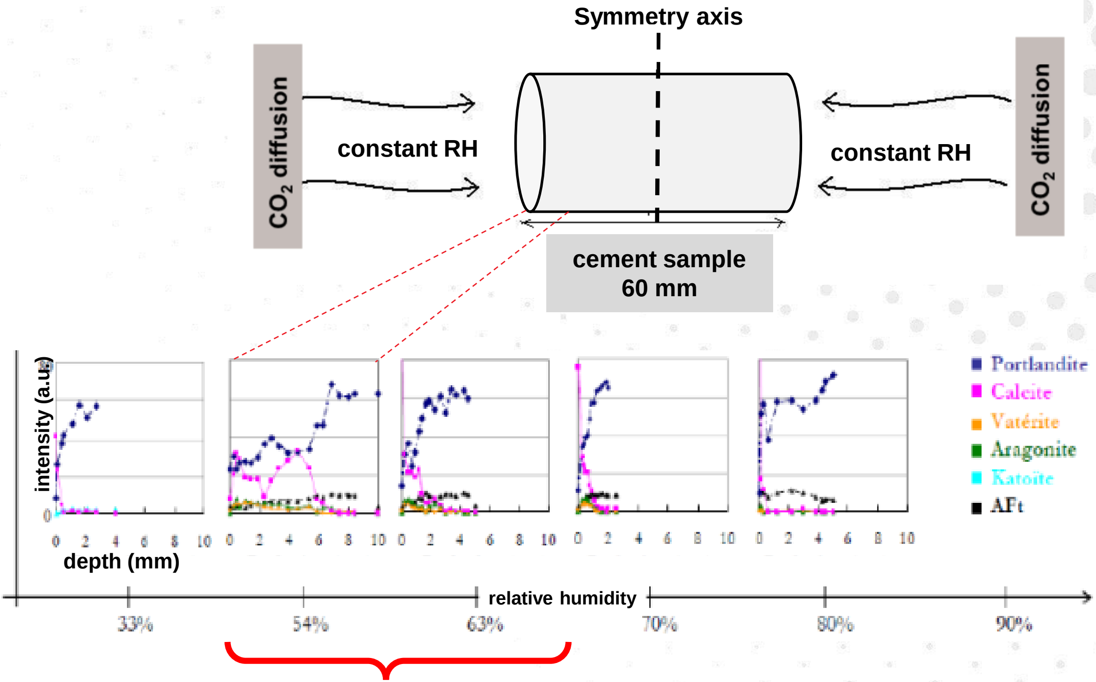


- ✓ Dissolution of CSH 1.6, ettringite, monocarboaluminate and hydrotalcite on 2 cm after 100 years
- ✓ Precipitation of CSH 1.2, CSH 0.8, straetlingite, amorphous silica and gypsum on the same thickness
- ✓ Precipitation of small amounts of sepiolite, gibbsite and katoïte-Si is also predicted

Modeling carbonation experiments : parameter calibration

MODELING ACCELERATED CARBONATION EXPERIMENTS

Experimental conditions: carbonation of CEM I cement paste at 20°C with $pCO_2 = 0.5$ bar; different experiments at constant RH = 33%, 54%, 63%, 70%, 80% (Drouet, 2010)



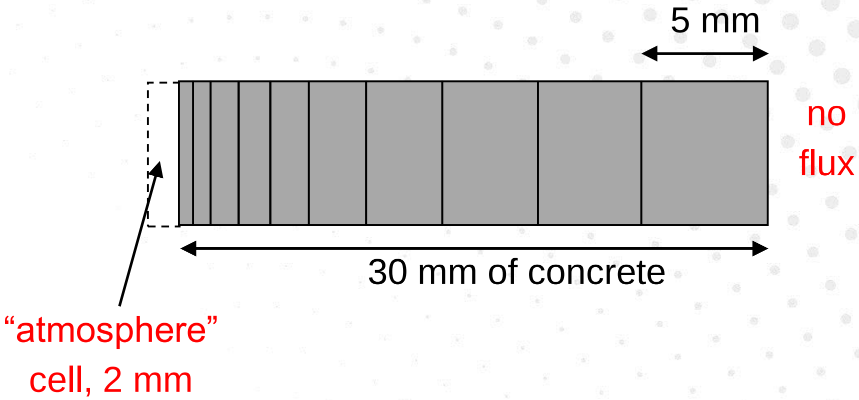
optimal carbonation (but not fully carbonated)

PARAMETER CALIBRATION WITH ACCELERATED CARBONATION EXPERIMENTS

Coupled reaction-transport modeling with Toughreact (EOS4):

1D Cartesian – 30 mm divided into 40 cells for the cement paste,

1 extra cell for “atmosphere”



Experiments with a CEM cement paste

	CEM I
Porosity	0.37
Intrinsic permeability to liquid (m²)	1e-19
Intrinsic permeability to gas (m²)	1e-17
Relative permeability m – Slr – Sls - Sgr	0.424 – 0.0 – 1.0 – 0.0
Capillarity pressure m – P_0 (MPa) – Pmax (MPa)	0.424 – 15 - 1500
Molecular diffusion coefficient in gaseous phase (m²/s)	2.4e-5
Molecular diffusion coefficient in aqueous phase (m²/s)	1.9e-9
Millington-Quirk a parameter	2
Millington-Quirk b parameter	4.2
Klinkenberg parameter (MPa)	0.45

coupling equation (Millington-Quirk relationship):

$$D_{eff} = D_0 \omega^a S_l^b$$

CHEMICAL REACTION PARAMETERS (1)

✓ Primary phases

Phase	Volume %
Calcite	1.4
Portlandite	24.3
CSH 1.6	55.4
Monocarboaluminate	7.0
Ettringite	11.9

✓ Secondary phases

Phase type	Phases
Oxides	Magnetite, Amorphous silica
Hydroxides	Brucite, Gibbsite, $Fe(OH)_3$
Sheet silicates	Sepiolite
Other silicates	CSH 1.2, CSH 0.8, Straetlingite, Katoite_Si
Sulfates, chlorides, other salts	Gypsum, Anhydrite, Burkeite, Syngenite, Glaserite, Arcanite, Glauberite, Polyhalite
Carbonates	Calcite, Nahcolite
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✓ Kinetics of dissolution / precipitation

$$r_n = \pm \boxed{k_n A_n} \left| 1 - \Omega_n^{\theta} \right|^{\eta} \qquad k_n(T) = k_{298{,}15} \exp\left[\frac{-E_a}{R} \left(\frac{1}{T} - \frac{1}{298{,}15} \right) \right]$$

CHEMICAL REACTION PARAMETERS (2)

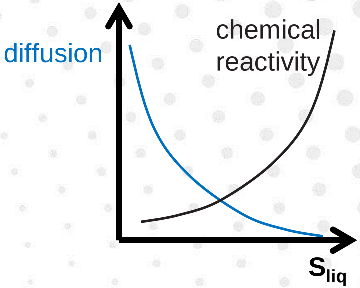
Primary and Secondary phases kinetics parameters

Phase	Kinétic Constant (298.15 K)	Activation Energy (kJ.mol^{-1})	Specific Surface (m^2.g^{-1})
C_3FH_6	$1\ 10^{-12}$	30	1
Calcite	$1.6\ 10^{-6}$	23.4	1
CSH 0.8	$1.6\ 10^{-9}$	50	1
CSH 1.2	$1.6\ 10^{-9}$	50	1
CSH 1.6	$1.6\ 10^{-9}$	30	1
Ettringite	$1.6\ 10^{-9}$	30	1
Gibbsite_am	$1.6\ 10^{-9}$	30	1
Gypsum	$1.6\ 10^{-5}$	20	1
Hydrotalcite	$1.6\ 10^{-9}$	30	1
Iron Hydroxyde	$1.6\ 10^{-8}$	30	10
Monocarboaluminate	$1.6\ 10^{-9}$	10	1
Portlandite	$1.6\ 10^{-8}$	20	1
Sépiolite	$1.6\ 10^{-12}$	50	10
Amorphous SiO_2	$1.6\ 10^{-9}$	30	1
Straetlingite	$1.6\ 10^{-9}$	50	1

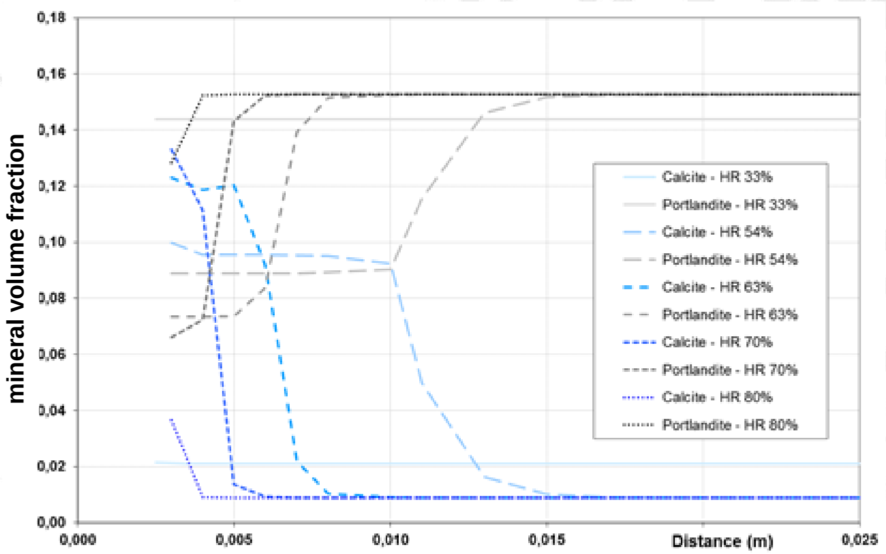
we added a coupling equation : chemical reactivity coefficient R_s

$$r_n' = R_s\, r_n$$

$$\boxed{0 \leq R_s(RH) \leq 1}$$



DIRECT CARBONATION MODELING RESULTS (MANUAL FITTING)



- ✓ calcite and portlandite profiles at 20 °C with
  k(CH) x 1.8 — k(CSH 1.6) x 0.1 — MQ parameters a = 2.6 and b = 5.4
  R_s = 0.10 – 0.70 - 0.95 - 1.00 (resp. for 33% - 54% - 70% - 80%RH)
- ✓ results are not completely satisfactory : carbonation fronts and effect of liquid saturation are not correctly predicted

INVERSE MODELING: BUILDING A GAUSSIAN PROCESS METAMODEL

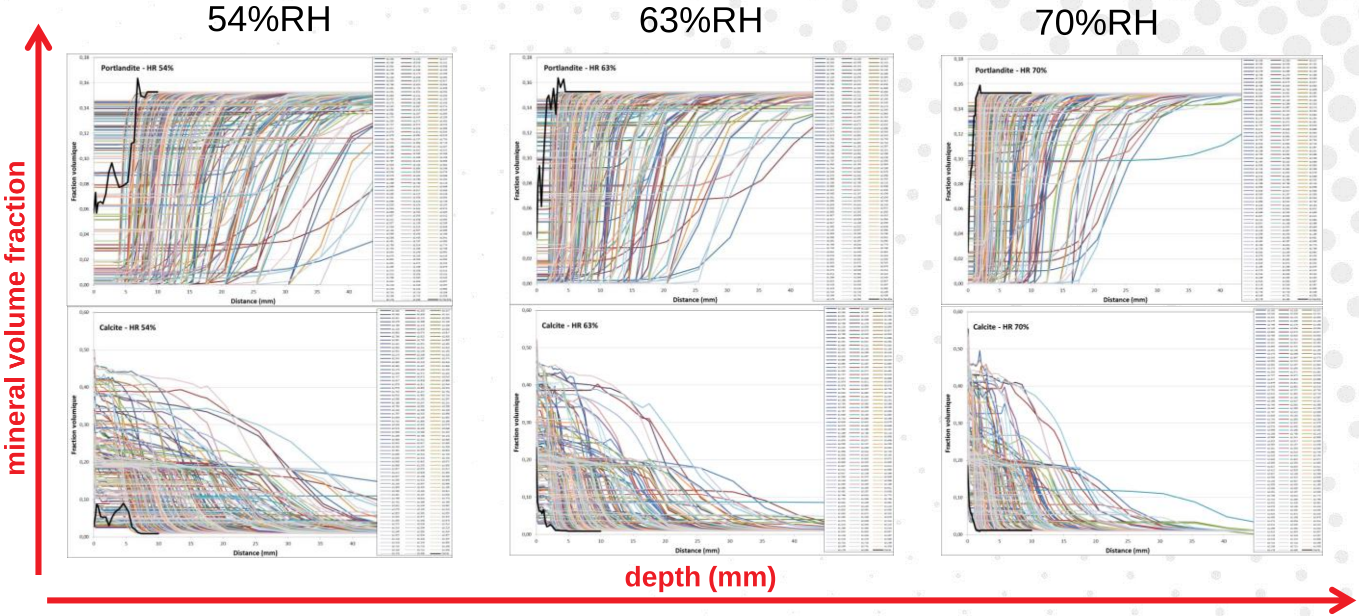
- ✓ use a kriging or Gauss processes (GP) metamodel to approximate the results of the numerical model (building an interpolated response surface)
- ✓ perform a "large" number of simulations (600) to build a "learning base" in a specified domain of variation for selected "uncertain" parameters (with uniform law)

Input parameters	**Minimal values**	**Maximal values**	**Reference values**
log k portlandite	-8.5	-6	-4.5
log k CSH 1.6	-11	-7	-8.8
log k ettringite	-11	-7	-8.8
Millington-Quirk a	1	3	2
Millington-Quirk b	2.1	6.3	4.2
Reactivity coefficient R_s	0.3	1	1

RESULTS OF THE GP METAMODEL

- ✓ the set of parameters are sampled using space-filling design (optimized LHS* method) which enables to efficiently explore the variation domain of parameters (*Latin Hypercube Sampling)

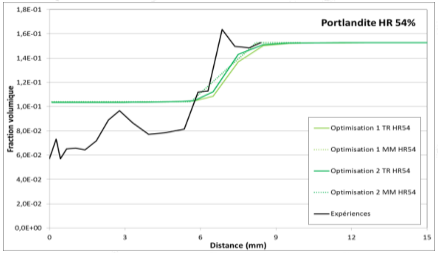
  ~~33%RH, 80%RH~~

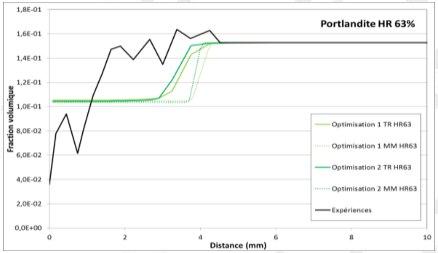


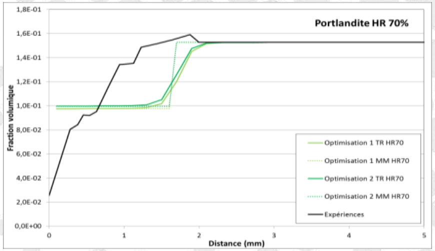
Experimental results (curves in black)

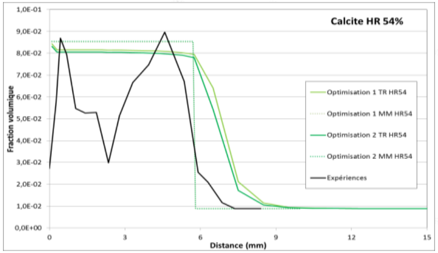
INVERSE MODELING TO FIT PARAMETERS

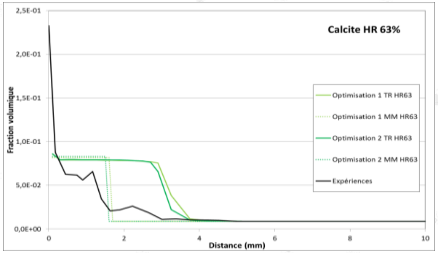
- ✓ GP metamodels are used to determine the optimal set of parameters that matches the experimental results (minimization of an objective function)

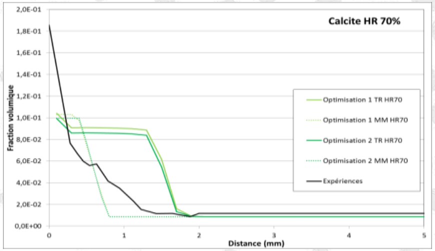












☺ GP metamodel predictions are quite good !

☹ Toughreact results are "less" satisfactory

Parameters		optimized value	reference value
X_1	log k portlandite	-7,41	**-7,8**
X_2	log k CSH 1.6	-8,71	**-8,8**
X_3	log k ettringite	-10,64	**-8,8**
X_4	Millington-Quirk *a*	2,69	**2**
X_5	Millington-Quirk *b*	6,43	**4,2**
X_6	Réactivité HR 54%	0,40	**1**
X_6	Réactivité HR 63%	0,33	**1**
X_6	Réactivité HR 70%	0,33	**1**

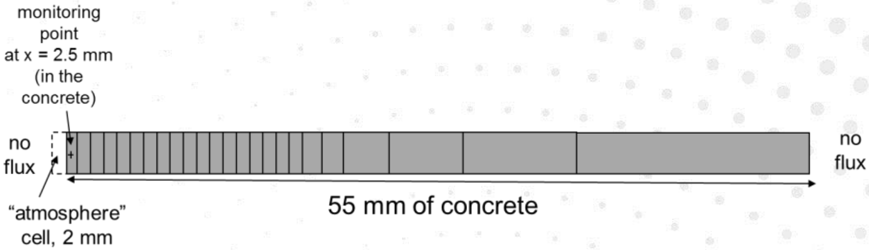
SUMMARY OF CALIBRATION RESULTS

- ✓ the global sensitivity analysis shows that:
  - ✓ the kinetics of portlandite is a key parameter
  - ✓ some parameters may play a role when interacting with others (secondary influence), e.g. diffusion parameters with portlandite or CSH1.6 dissolution kinetics
  - ✓ the reactivity parameter is not very influential (counter-intuitive result!)

Modeling concrete carbonation : a benchmarking exercise

BENCHMARK : GEOMETRY AND COMPONENTS

1D Cartesian – 5.5 cm divided in 11 cells (5 mm) for **HPC**
1 extra cell for “atmosphere”



very low aqueous diffusivity $k_{rl} = 0; k_{rg} = 1$
constant porosity

Components :

1. drying process
2. carbonation at constant liquid saturation
    - a. CH + calcite
    - b. Complete mineralogy
3. coupled drying and carbonation
    - a. CH + calcite
    - b. Complete mineralogy

Full multiphase codes

Toughreact (CEA + T. Xu, JLU)

HYTEC (in progress)

Drying with Richards’ equation

HYTEC (N. Seigneur, Mines Paristech)

Crunchflow (CEA + C. Steefel, LBNL)

PFLOTRAN (P. Alt-Epping, Uni Bern)

CHEMICAL REACTION PARAMETERS (1)

- ✓ Primary phases

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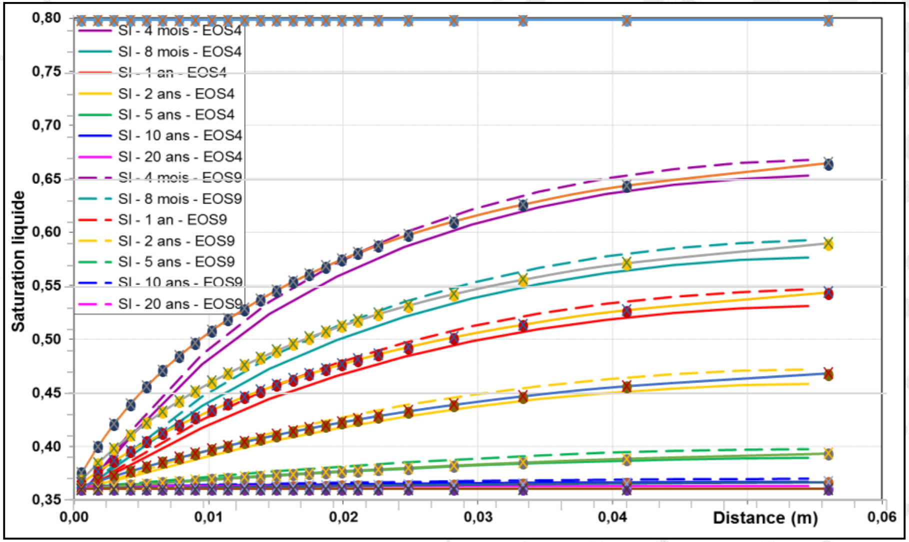
BENCHMARK : COMPONENT 1: DRYING RESULTS



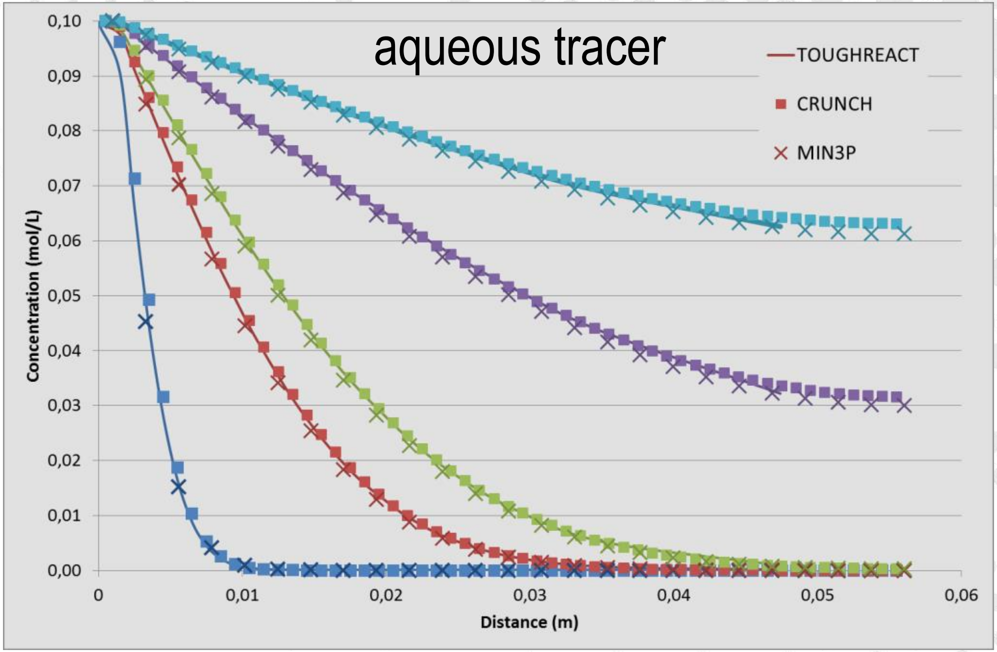
TOUGH2 - Full multiphase (EOS4)
TOUGH2 - Richards (EOS9)
FLOTRAN - PFLOTRAN

→ OK to use Richards' equation for benchmarking exercise

Making sure the same effective diffusion coefficient is used…

coupling equation
(Millington-Quirk relationship):

$$D_{eff} = D_0 \omega^a S_l^b$$



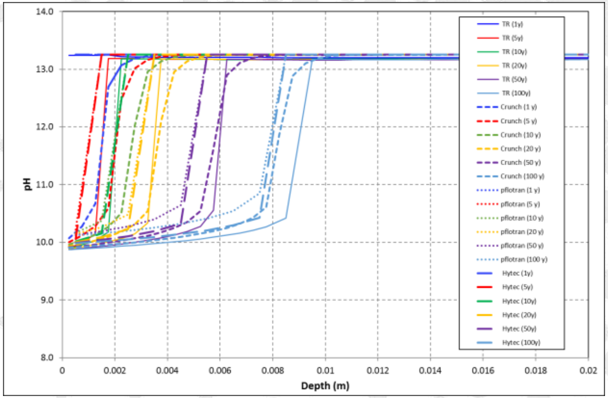
For Crunchflow, b = 3.2 has to be used
(instead of b = 4.2 for Toughreact)

BENCHMARK :
COMPONENT 2A: PORTLANDITE CARBONATION AT CONSTANT S_L

Portlandite and Calcite only

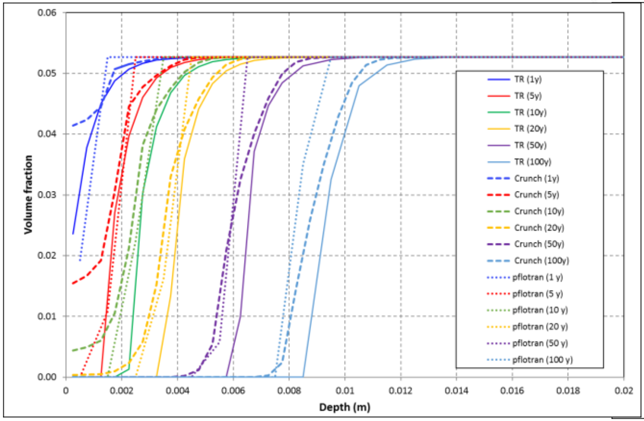
Some discrepancies are observed in this simplified case…

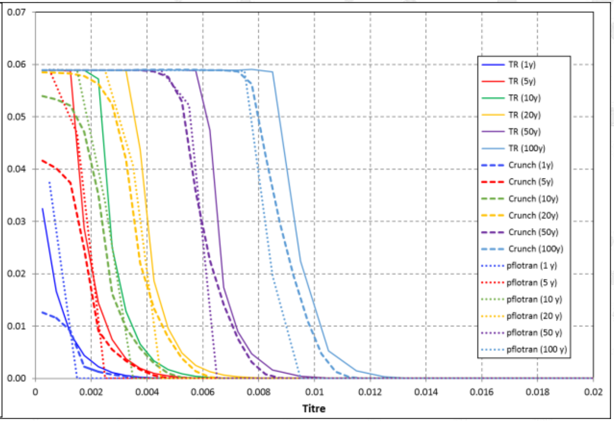
pH



Portlandite

Calcite



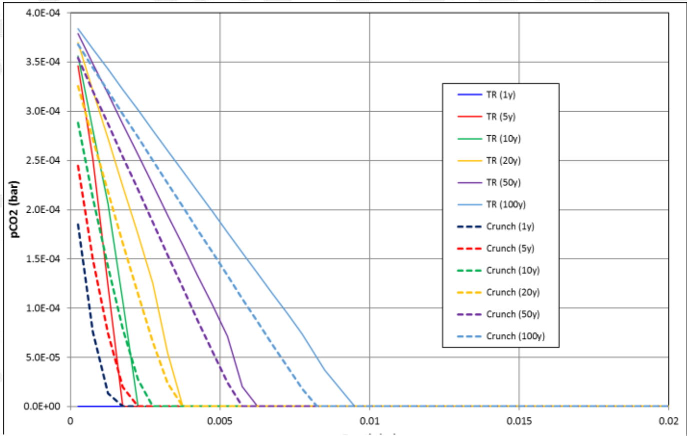


BENCHMARK : COMPONENT 2A: PORTLANDITE CARBONATION AT CONSTANT S_L

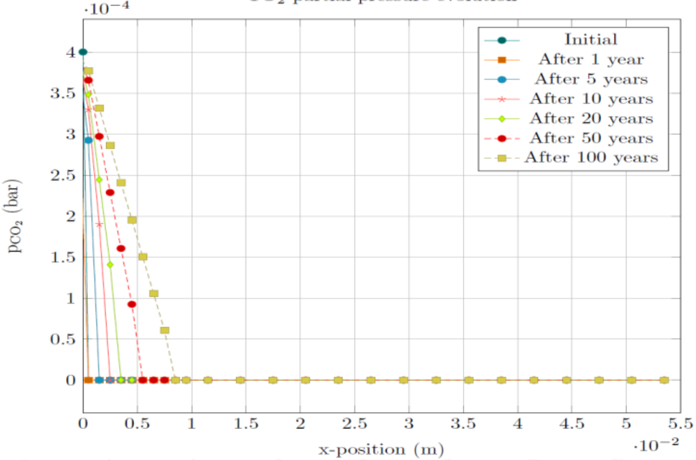
Portlandite and Calcite only

Some discrepancies are observed in this simplified case…

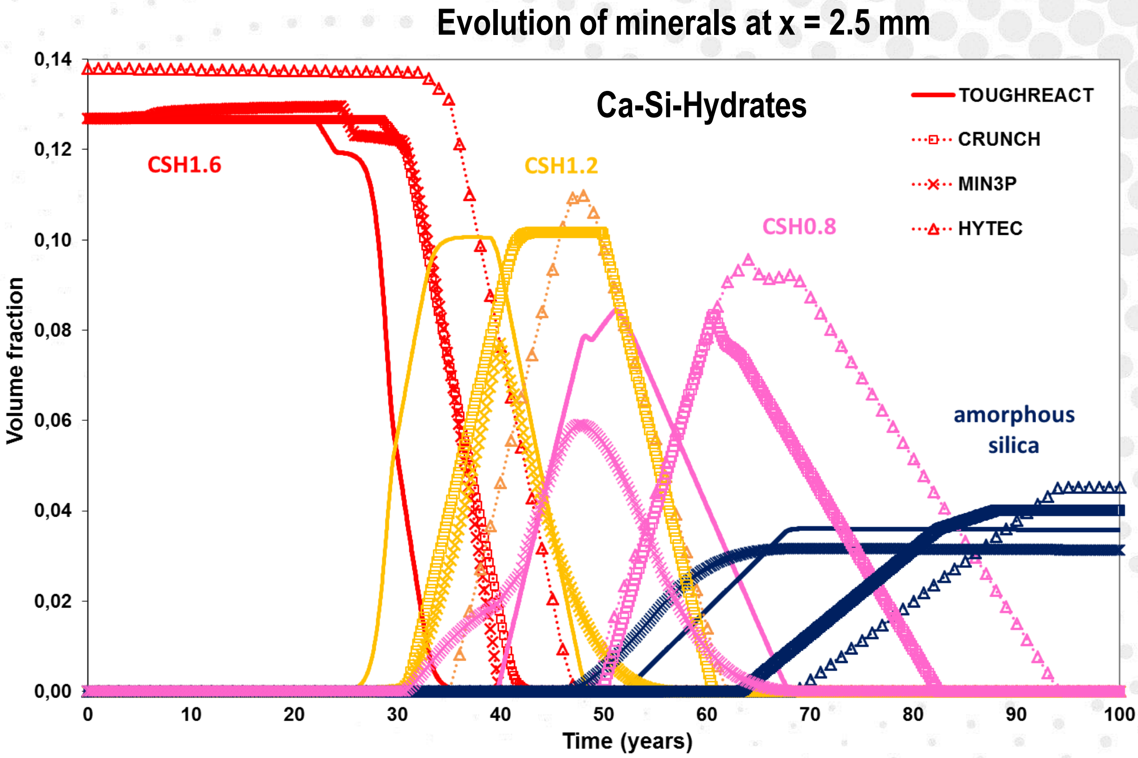
pCO_2



CO_2 partial pressure evolution



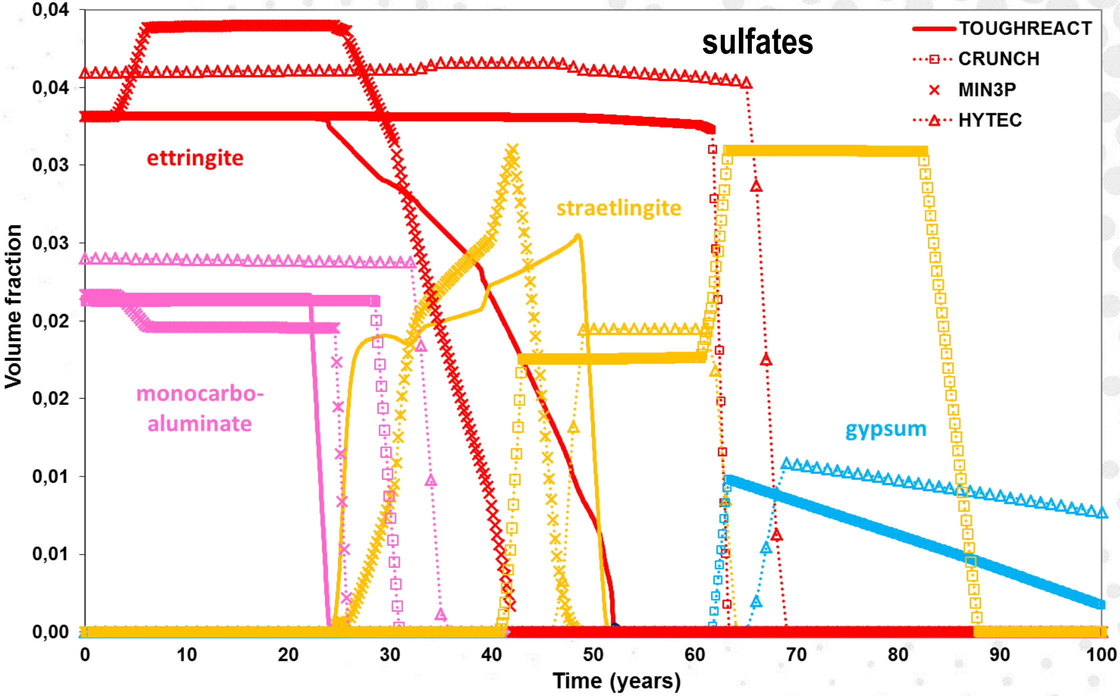
BENCHMARK :
COMPONENT 2B: CONCRETE CARBONATION AT CONSTANT S_L



Same mineral paragenesis but timing not exactly the same for all codes

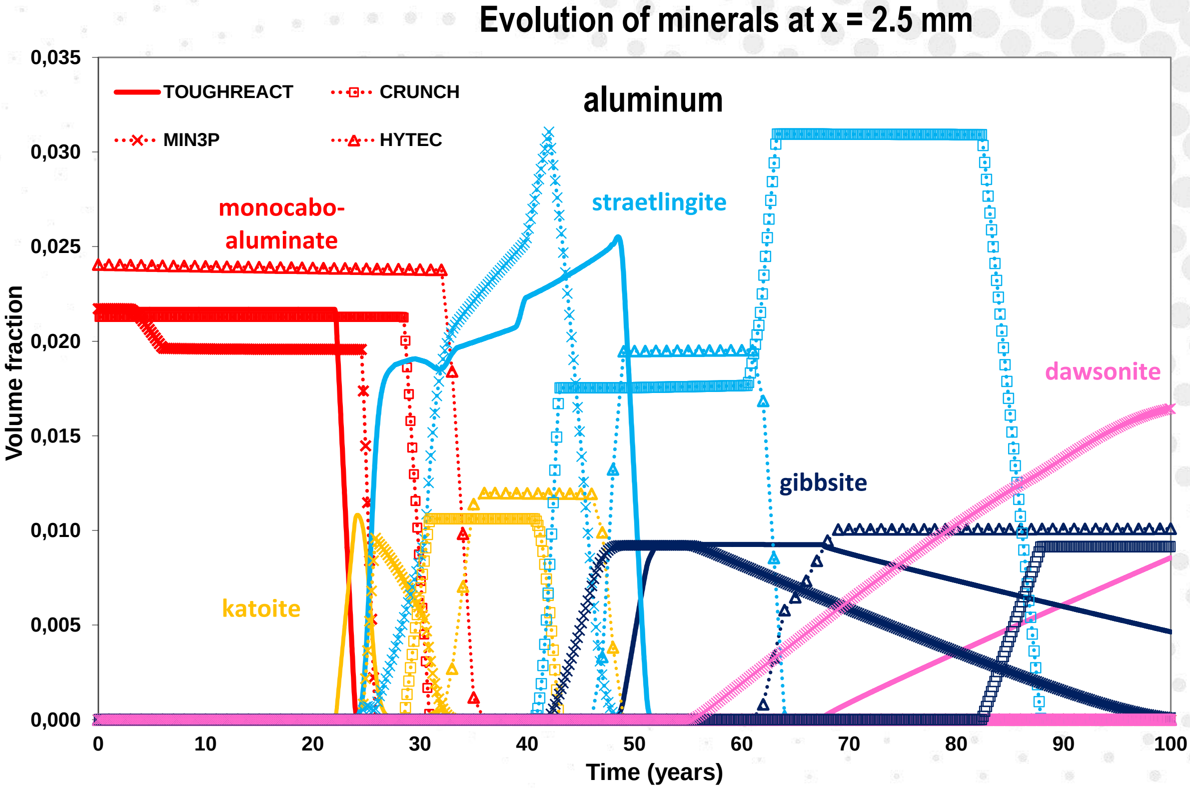
BENCHMARK :
COMPONENT 2B: CONCRETE CARBONATION AT CONSTANT S_L

Evolution of minerals at x = 2.5 mm



Precipitation of gypsum in the simulation with Crunchflow and Hytec

BENCHMARK :
COMPONENT 2B: CONCRETE CARBONATION AT CONSTANT S_L



Dawsonite does not precipitate with Crunchflow and Hytec
Straetlingite more persistent with Crunchflow

CONCRETE CARBONATION BENCHMARK SUMMARY

- ✓ Concrete carbonation benchmark exercise
  - ✓ differences between codes do not seem to be linked to the grid size or coupling method
  - ✓ differences in results attributable to transport in the gas phase?
  - ✓ CPU concerns: no SIA → small time steps → CPU times go up !
- ✓ Component 2a-3a with simplified chemistry
- ✓ Component 3 with fully coupled drying+carbonation only with Toughreact
- ✓ New component : variable porosity, corrosion ?

Thank you for your attention

Acknowledgment

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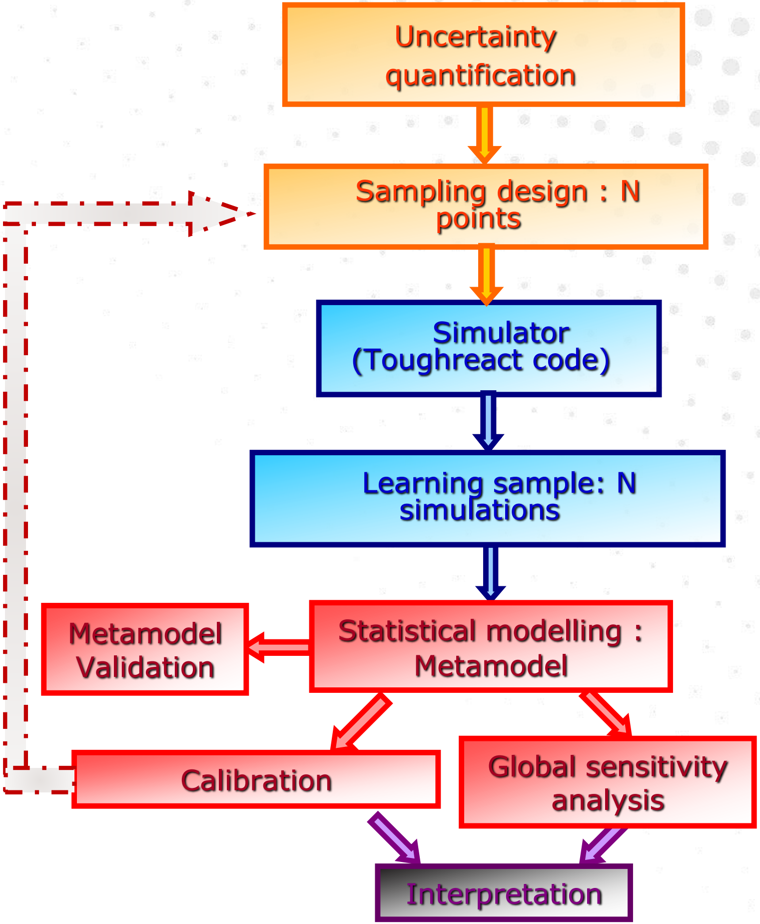
STOCHASTIC APPROACH FOR CALIBRATION



Uncertainty quantification

Sampling design : N points

Simulator (Toughreact code)

Learning sample: N simulations

Metamodel Validation

Statistical modelling : Metamodel

Calibration

Global sensitivity analysis

Interpretation

- **Uncertainty quantification :**

  Domain of variation *of uncertain parameters*

- **Sampling design :**

  Latin Hypercube Sample *with optimal recovering properties*

- **Metamodel :**

  Replace Toughreact code with a faster surrogate model, called metamodel ⇒ ***Gaussian process metamodels for 3 curve indicators***

- **Sensitivity analysis :**

  Computation of ***Sobol indices*** *(variance-based importance mesures)*

- **Calibration :**

  metamodels used to determine ***the optimal set of parameters*** *that matches the experimental results*
  (by minimizing an objective function)

GLOBAL SENSITIVITY ANALYSIS

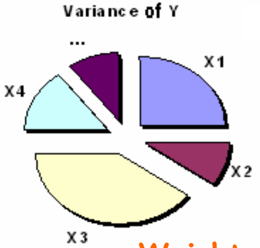
- **Sensitivity analysis** : "Study of influence of inputs on the output of the simulator" *Saltelli [1999]*

- Global Sensitivity Analysis (GSA) based upon variance decomposition:

$$\mathbf{Var}(Y) = \sum_{i=1}^{d} V_i(Y) + \sum_{i<j}^{d} V_{ij}(Y) + \cdots + V_{12\cdots d}(Y)$$

Primary effect of X_i

Interaction effect between X_i and X_j



Weight of input uncertainties on the output

$$S_i = \frac{V_i}{Var[Y]}$$

index: *Influence of an input, independently from the others*

$$S_{Ti} = S_i + \sum_{\substack{1\le j\le d \\ j\ne i}} S_{ij} + \sum_{\substack{1\le j,k\le d \\ j\ne i, k\ne i}} S_{ijk} + \ldots$$

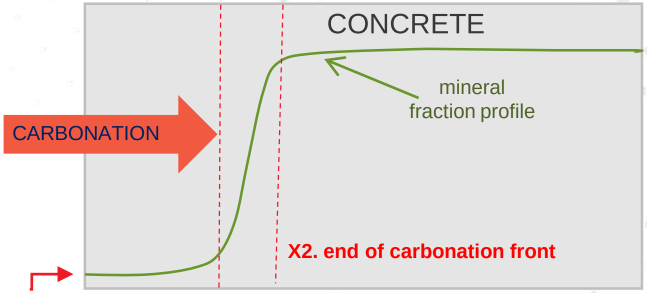
l **index:** *total influence of an input and all its interactions*

Estimation techniques: Monte Carlo (MC) based upon random sampling

Several thousands of simulations required ⇒ use of the GP metamodels

ASSESSING GP METAMODEL QUALITY

- ✓ GP metamodel is built for 3 indicators (characteristic of the output curves) and the GP quality is assessed using predictivity coefficients Q^2 (Saporta 2006)



Y_{init}: mineral quantity at the surface of the concrete

X1. beginning of carbonation front

Q^2	Y_{init}	X_1	X_2
HR 54% - Portlandite	0,99	0,89	0,94
HR 54% - Calcite	0,98	**0,40**	0,85
HR 63% - Portlandite	0,99	0,93	0,95
HR 63% - Calcite	0,98	**0,56**	0,82
HR 70% - Portlandite	0,99	0,85	0,919
HR 70% - Calcite	0,98	**0,39**	0,90

- ✓ Q^2 values are high for Y_{init} and for X_2
- ✓ Q^2 values are low for X_1 for calcite1

→ overall quality is good

SENSITIVITY ANALYSIS

- ✓ the influence of the different parameters is determined using Sobol indices (based on variance decomposition) (Sobol 1993)
- ✓ Estimation of Sobol indices with GP metamodels and Monte Carlo approach

Sobol index for	log k portlandite	log k CSH 1.6	log k calcite	M.Q. a	M.Q. b	Reactivity
HR 54% - Portlandite						
1. value at surface	**0.9043** **0.9669**	0 0.0013	0 0.0013	0 0.0013	0 0.0029	0.0328 0.0960
2. value at depth	0.0736 **0.5273**	0 0.0324	0 0.0325	0.0795 **0.4207**	0.2222 **0.7341**	0.0123 0.1765
3. front position	**0.5951** **0.8510**	0.0017 0	0.0069 0.0372	0.0113 0.0277	0.0335 0.1535	0.0748 0.2440
HR 54% - Calcite						
1. value at surface	**0.4093** **0.4171**	**0.3861** **0.4099**	0 0	0 0	0.0015 0	0.1468 0.1788
2. value at depth	0.0063 **0.4748**	0 0.0026	0 0.0026	0.0960 **0.5867**	**0.3506** **0.8040**	0.0025 0.0089
3. front position	0.2264 **0.7016**	0.0041 0.2572	0.006 0	0.0048 0.0205	0.0241 0.2109	0.1755 **0.5181**

direct effect

effect with interactions

no effect!!