



Water Sorption of cement paste: Effect of temperature & carbonation

Stéphane POYET

DE LA RECHERCHE À L'INDUSTRIE

International workshop on mechanisms of concrete carbonation (Concarb2019)
Champs-sur-Marne (France), June 27, 2019

Commissariat à l'énergie atomique et aux énergies alternatives - www.cea.fr

Radioactive waste management

- ▶ Intermediate level waste (ILW) & Intermediate long-lived waste (ILW-LL)
 - ▶ Waste packages and structure elements would be subjected to CO₂ and heat (thermal output of the waste)
 - ▶ It is necessary to be account for the influence of temperature and carbonation on water retention and transport
- Durability assessment of waste packages and concrete structures

Outline of the presentation

- ▶ Influence of temperature on water sorption
- ▶ Influence of carbonation on water sorption and transport

4 hardened cement pastes

- ▶ Use of 4 different binders with siliceous SCMs
- ▶ Common w/b ratio = 0.40
- ▶ Curing = 4 months under artificial pore solution

Paste	PI	PV	PIII	T1
Binder	OPC	CEM V/A	CEM III/A	LAC
OPC	100%	56%	39%	37.5%
SCMs		22% S + 22% FA	61% S	30% FA + 32.5% SF

S = Slag
FA = Fly Ash
SF = Silica Fume

→ + SCMs Porosity

Porosity	36%	37%	40%	41%
[CH] (mol/L of paste)	5.4	2.3	1.8	0.0
[C-S-H] (mol/L of paste)	5.2	6.5	6.5	7.6

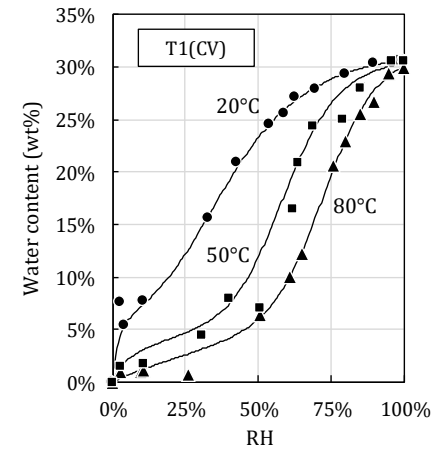
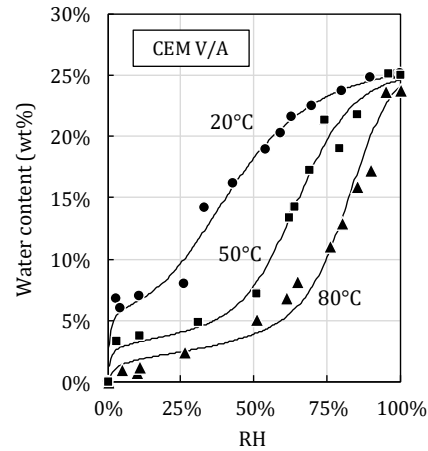
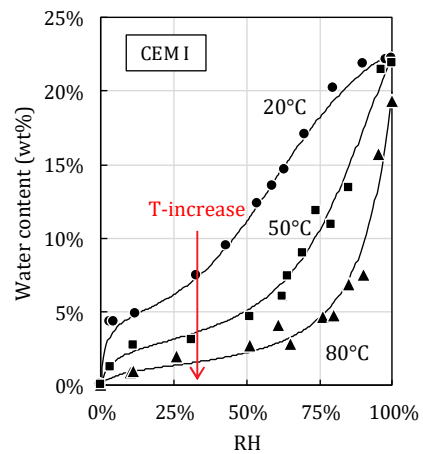
Approx.

[CH] + ← → + [C-S-H]

Desorption isotherm - Water content (wt%) versus RH

- ▶ Desorption isotherms at **20, 50 & 80°C**
- ▶ Use of the desiccator method (saturated salt solutions)
- ▶ Significant modifications due to temperature:
 - 1) significant decrease in water retained
 - 2) modification of the desorption isotherm itself→ microstructure modification?

$$w(\text{wt}\%) = \frac{m(\text{water})}{m(\text{dry solid})}$$

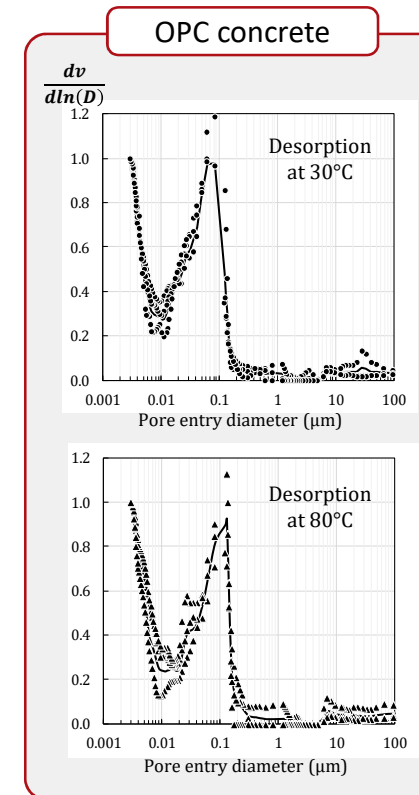


What happens?

- ▶ Use of Mercury Intrusion Porosimetry (MIP) → microstructure
- ▶ Use of OPC concrete (w/c = 0.43) tested for desorption at **30°C** and **80°C**
- ▶ The MIP results do not display significant differences
 - Modification of the microstructure was not thought to be the main reason for the T-induced changes
 - Another mechanism was believed to be at work

Thermal desorption

- ▶ Shift of equilibrium between vapour and adsorbed water induced by T
- ▶ Le Chatelier's principle: "the effect of a change in temperature on a system at equilibrium is to shift the equilibrium in the direction that acts to counteract the temperature change"
- ▶ Adsorption is an **exothermic process**
 - A temperature increase then promotes desorption
 - Water molecules are released and water content decreases



Modelling approach

- ▶ Assumption: no change in microstructure induced by temperature
(→ the effect of microstructure changes are neglected in front of thermal desorption)
- ▶ Use of Clausius-Clapeyron equation to account for the heat exchanged during adsorption

$$q_{st}(w) = -R \left[\frac{\partial \ln(p_v)}{\partial \left(\frac{1}{T}\right)} \right]_w$$

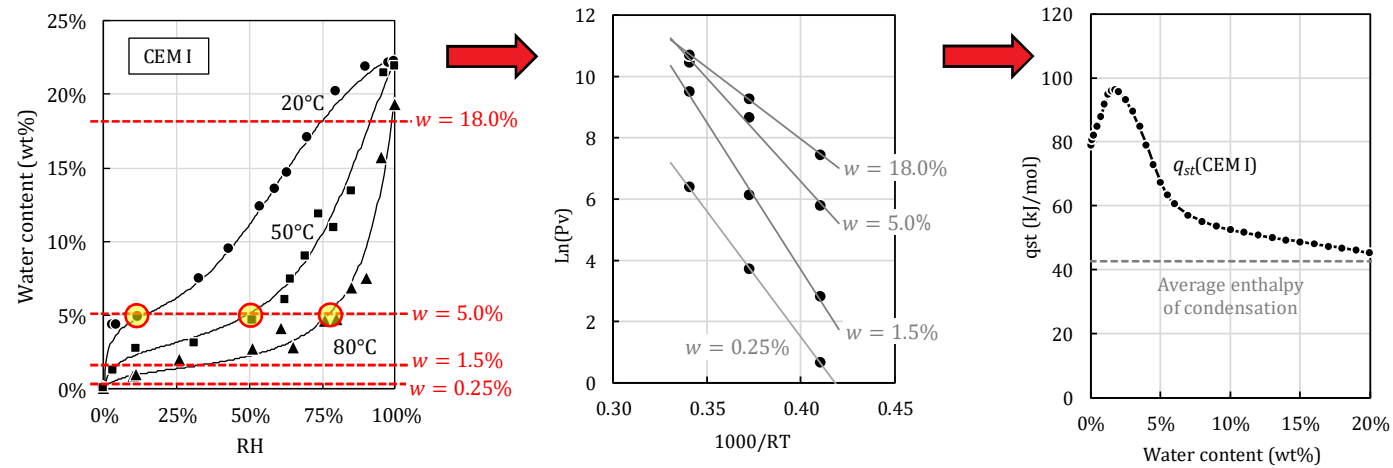
$\left\{ \begin{array}{l} q_{st} \text{ isosteric energy of adsorption for } w \text{ (kJ/mol)} \\ p_v \text{ vapour pressure at equilibrium with } w \text{ and } T \text{ (Pa)} \\ T \text{ absolute temperature (K)} \\ w \text{ water content} \end{array} \right.$

- ▶ $q_{st} \rightarrow$ slope of the curves $\{ \ln(p_v) - (1/T) \}$ at **constant water content values w**

Evaluation of the isosteric energy q_{st}

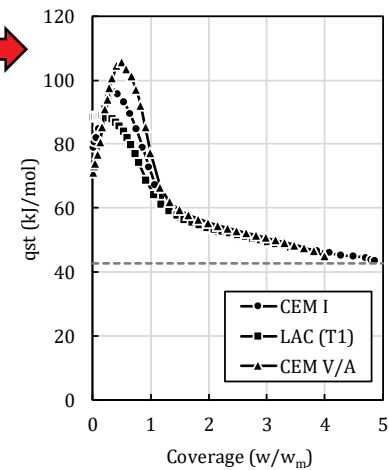
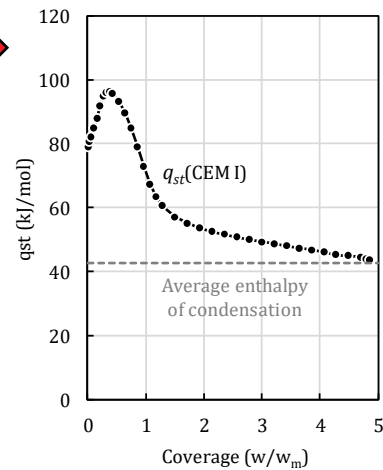
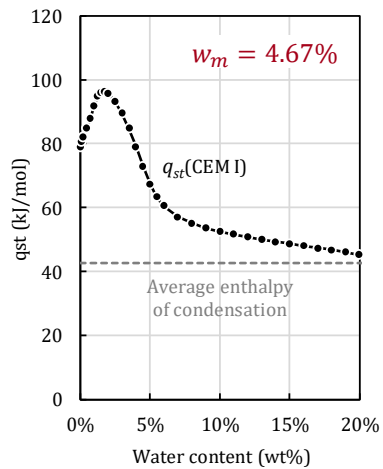
- ▶ Use of the experimental desorption isotherms (20, 50 and 80°C)
- ▶ Use of Clausius-Clapeyron
- ▶ Use of a model to fit the isotherm and evaluate $p_v(w, T) = h(w, T)p_{vs}(T)$
- ▶ Example of the CEM I paste

$$q_{st}(w) = -R \left[\frac{\partial \ln(p_v)}{\partial \left(\frac{1}{T}\right)} \right]_w$$



Evaluation of the isosteric energy q_{st}

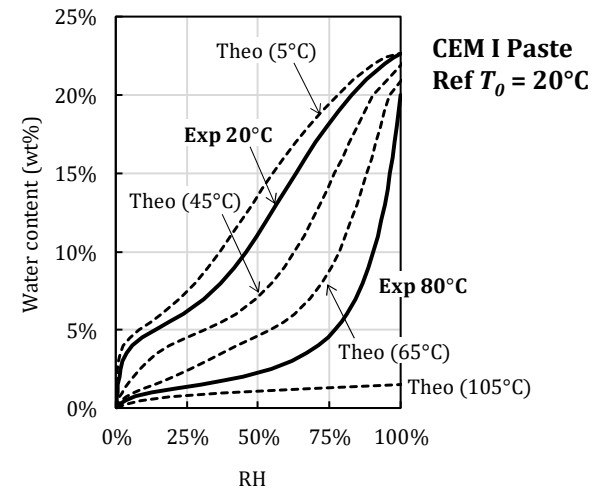
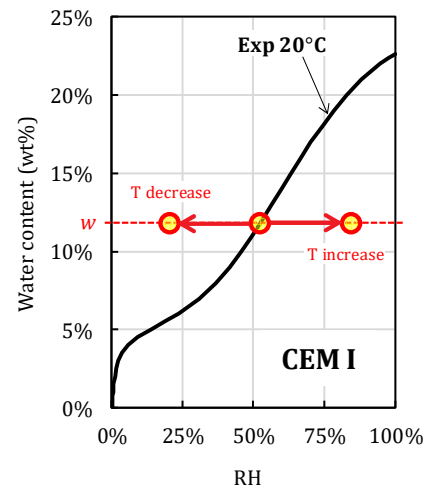
- ▶ Because the pastes present different microstructures the q_{st} results cannot be compared directly
- ▶ Coverage = w/w_m
with w_m = water content needed to complete the monolayer
→ Coverage \approx number of adsorbed water layers
- ▶ $w/w_m \leq 1 \rightarrow$ high energy of adsorption = influence of the substrate
→ But great uncertainties (at least ± 15 kJ/mol)...

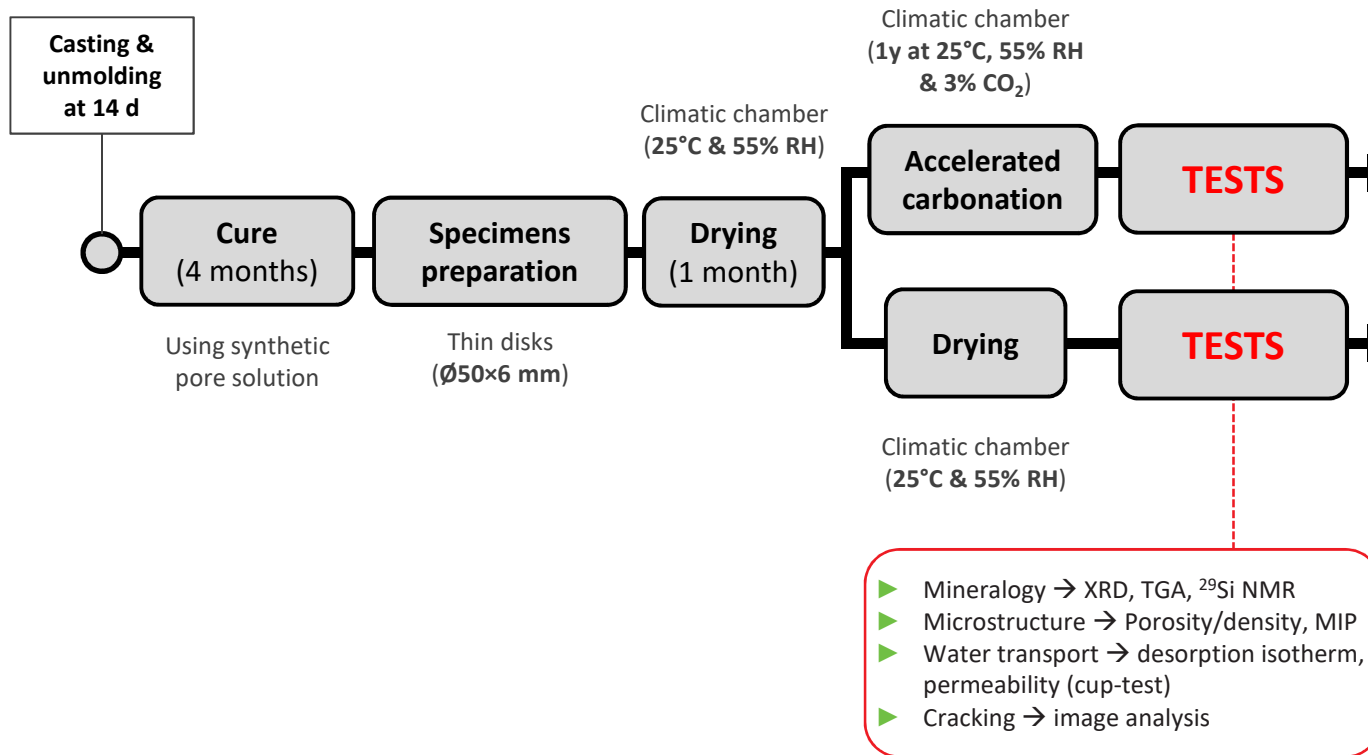


Assessment of the influence of temperature

- ▶ Integration Clausius-Clapeyron eq. between two different temperatures
 - Reference T_0 at which the desorption isotherm is known
 - Arbitrary T at which the desorption isotherm is to be evaluated
- ▶ Estimation of the shift of equilibrium in terms of RH h

$$q_{st}(w) = -R \left[\frac{\partial \ln(p_v)}{\partial \left(\frac{1}{T}\right)} \right]_w \Rightarrow h(w, T) = h(w, T_0) \frac{p_{vs}(T_0)}{p_{vs}(T)} \exp \left[q_{st}(w) \left(\frac{T - T_0}{RTT_0} \right) \right]$$



Methods → accelerated carbonation at 3% CO₂ (1y)

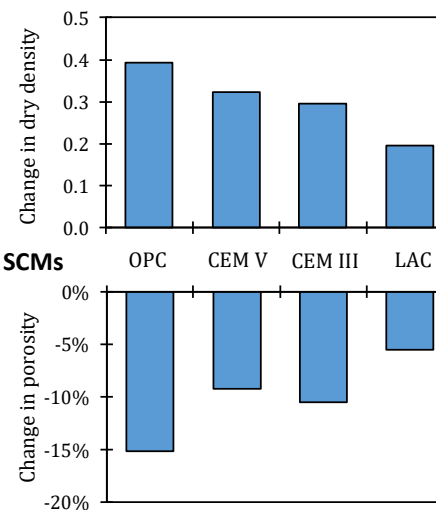
Impact of carbonation on porosity / density

- ▶ Incorporation of exogenous CO₂
 - increase in density
 - decrease in porosity
- ▶ The changes in porosity / density depend on the binder
 - differences in Ca-contents, degree of hydration...

Density (dry)	OPC	CEM V/A	CEM III/A	LAC (T1)
Non carbonated	1.69	1.56	1.60	1.36
Carbonated	2.08	1.88	1.90	1.56
Difference	+ 0.39	+ 0.32	+ 0.30	+ 0.20

[Ca] + ←————→ + SCMs

Porosity	OPC	CEM V/A	CEM III/A	LAC (T1)
Non carbonated	36%	37%	40%	41%
Carbonated	21%	28%	29%	36%
Difference	- 15%	- 9%	- 11%	- 5%

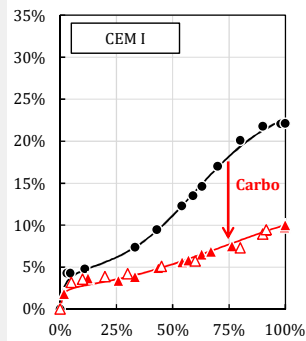


Desorption isotherm at 20°C - Water content (wt%) versus RH

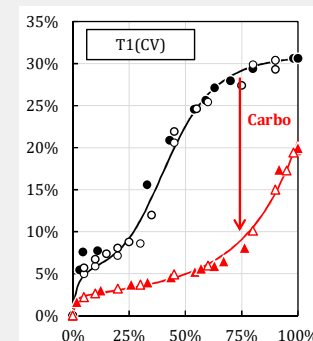
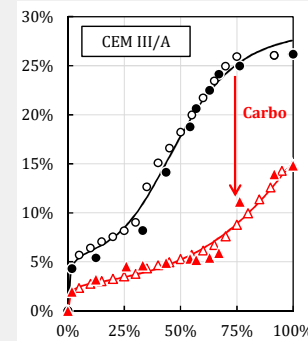
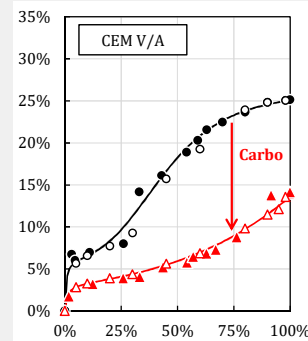
- ▶ Significant decrease in water content after carbonation, due to
 - 1) decrease in porosity → decrease in the amount of water retained
 - 2) increase in solid density → increase in the mass of dry solid
- ▶ Similar conclusions for all the binders → consistent with literature

$$w(\text{wt}\%) = \frac{m(\text{water})}{m(\text{dry solid})}$$

Portland cement



Blended cements

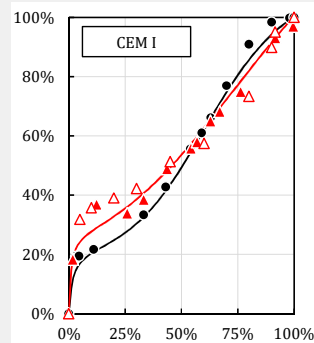


Desorption isotherm at 20°C – Saturation versus RH

$$S(\text{vol}\%) = \frac{v(\text{water})}{v(\text{porosity})}$$

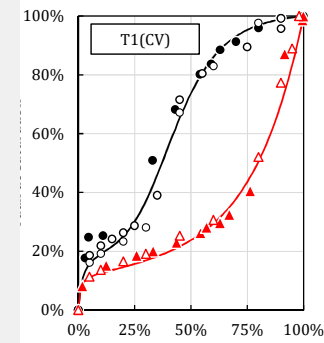
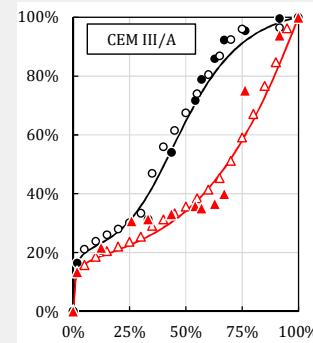
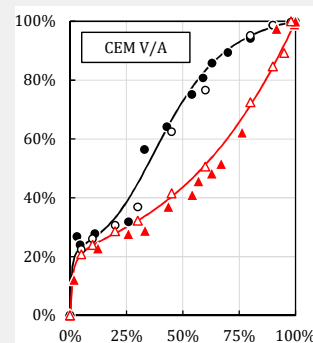
Portland cement

- ▶ The desorption isotherm after carbonation remains more or less unmodified
→ Similar to Houst (1992)
- ▶ Despite changes in porosity, the PSD is not expected to be modified



Blended cements

- ▶ Significant change in the desorption isotherms:
 - Decrease at low RH (decrease of pore surface)
 - Change at high RH (steeper curve)
→ creation of pores desaturated at high RH = coarsening of the pore-structure
- ▶ Similar conclusions for all the blended cements

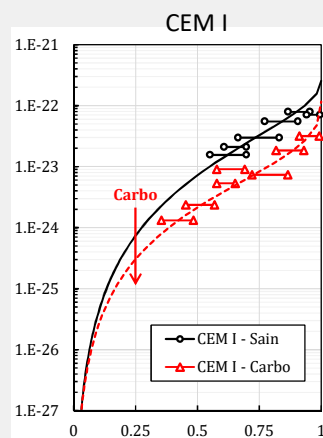


Effective permeability ($K_e = K_i \times k_{r,i}$) versus saturation (S)

- ▶ Cup-method + inverse analysis

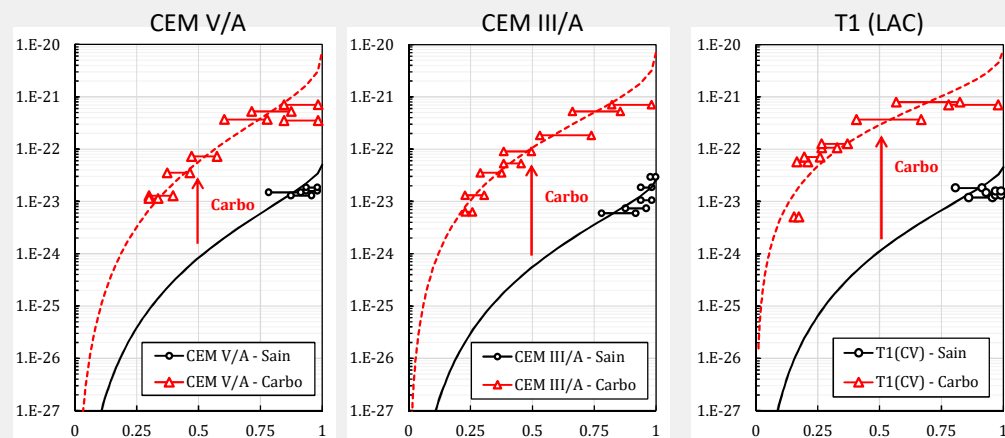
Portland cement

- ▶ Decrease in K_e induced by (accelerated) carbonation by a factor of 2
- Consistent with literature



Blended cements

- ▶ Significant increase in K_e induced by (accelerated) carbonation
- ▶ Increase of 2 orders of magnitude
- ▶ The increase depends on the considered binder
- Origin: coarsening of the pore-structure?

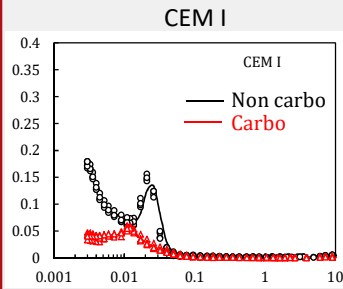


Pore size distribution (PSD) $\rightarrow \frac{dv}{d\ln(D)}$ vs. pore entry diameter (D)

- ▶ Use of mercury intrusion porosimetry
- ▶ Immersion into liquid N₂ + freeze-drying

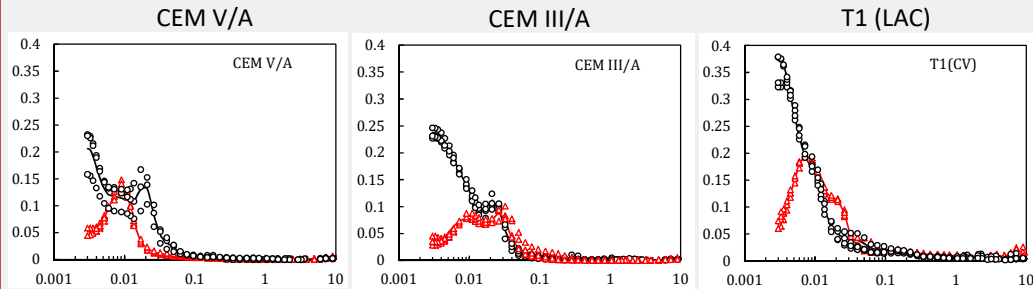
Portland cement

- ▶ No coarsening of the pore-structure after carbonation (as expected)
- Mainly porosity clogging



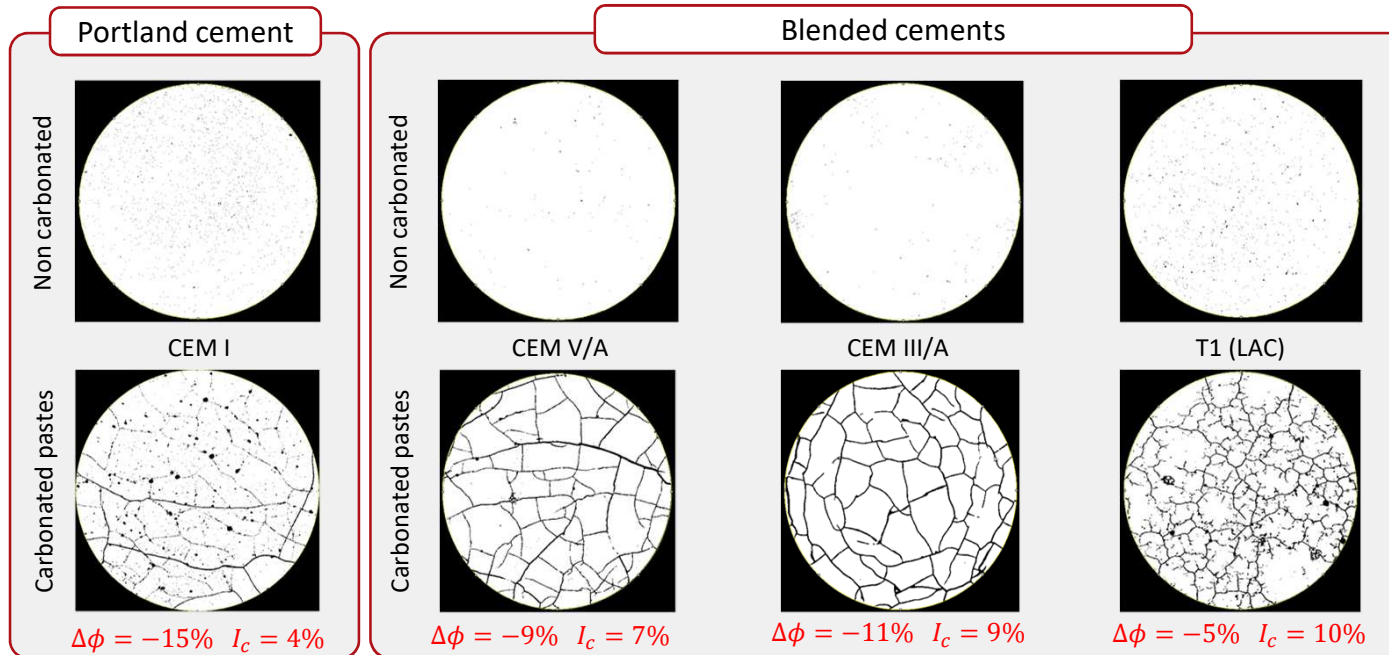
Blended cements

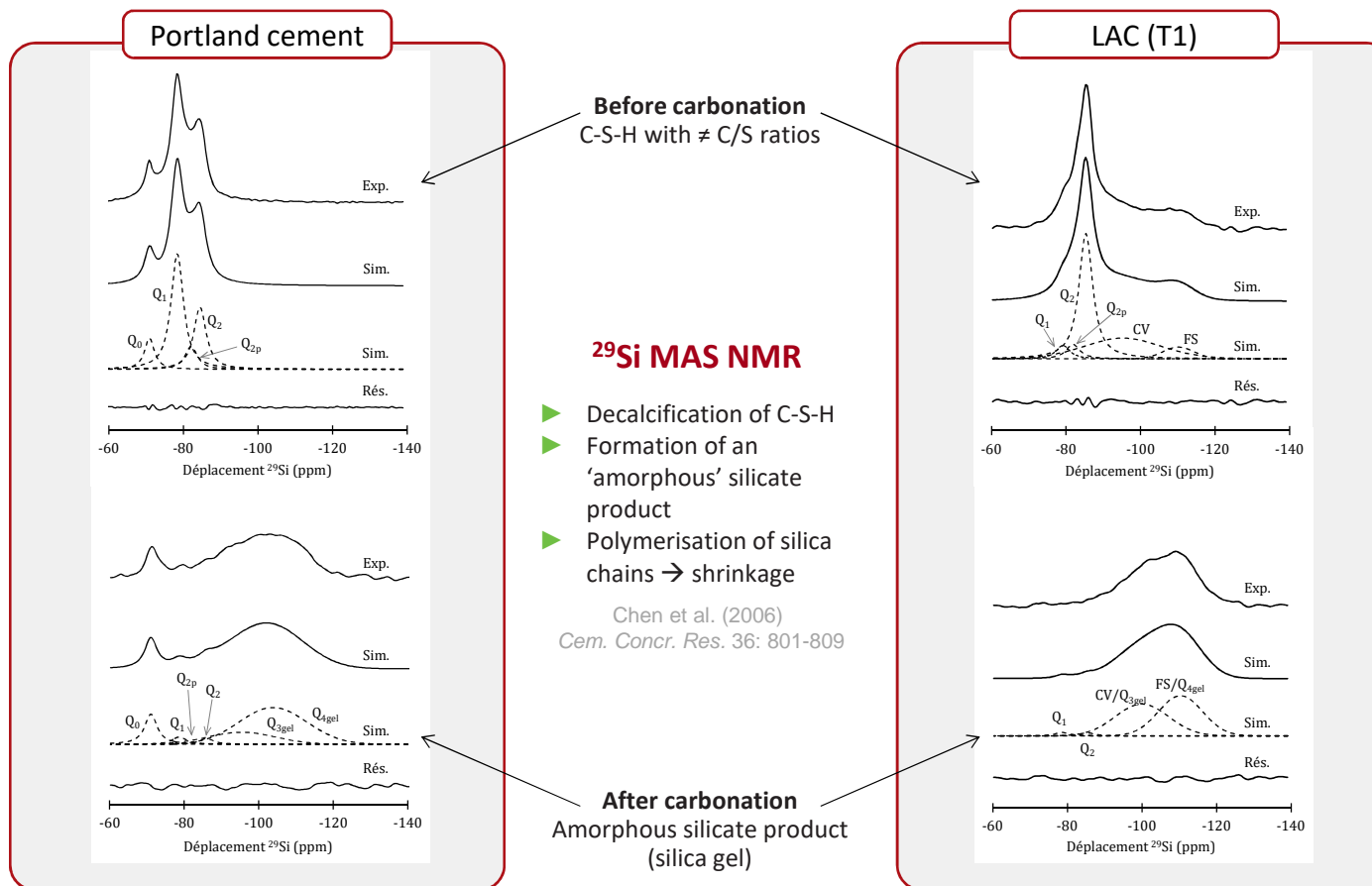
- ▶ No significant coarsening of the pore-structure after carbonation
- Mainly porosity clogging



Cracking → Image analysis

- ▶ Use of UV-fluorescent resin
 - ▶ Significant cracking after (accelerated) carbonation
 - ▶ Image analysis → I_c = surface fraction of cracks
- Competition between clogging and cracking





Are these results representative of natural carbonation?

- ▶ Comparison between 2 'similar' pastes

Natural carbonation

- ▶ Pastes prepared in **1994** Gallé & Daian (2000)
- ▶ CEM V/A with **w/c = 0.45** Mag. Concr. Res. 52
- ▶ Cylinders $\varnothing 40 \times 80$ mm 251-263
- ▶ Specimens kept in the laboratory at ambient conditions without protection against CO_2
- ▶ Carbonation depth ≈ 10 mm

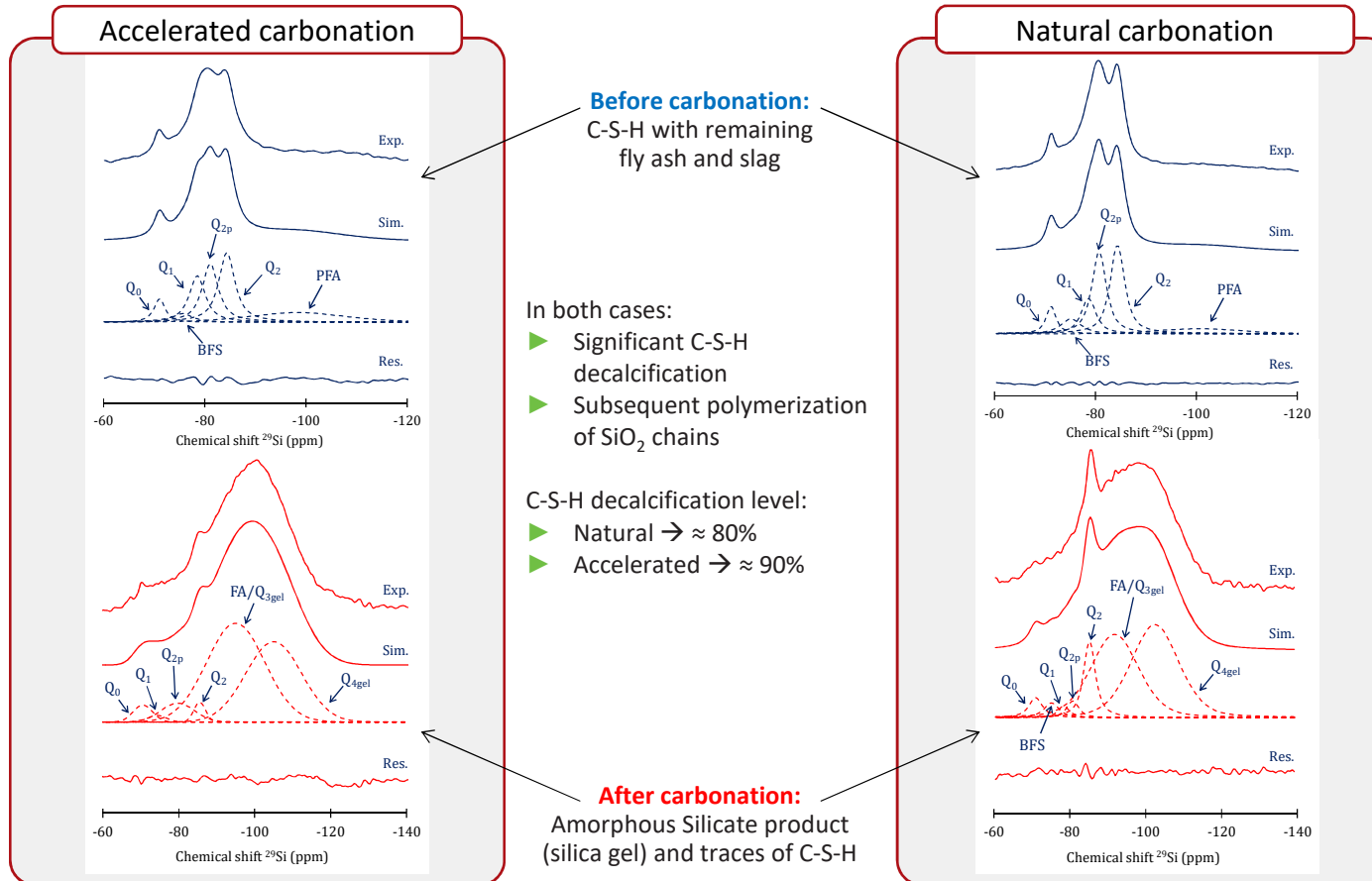


Phenolphthalein on a fresh cross-section

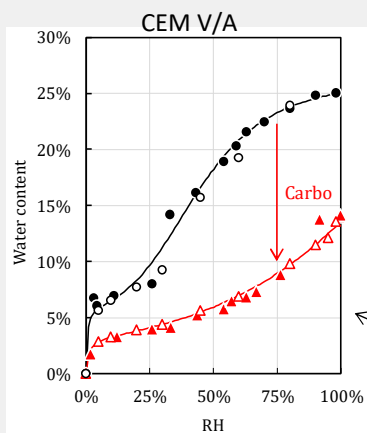
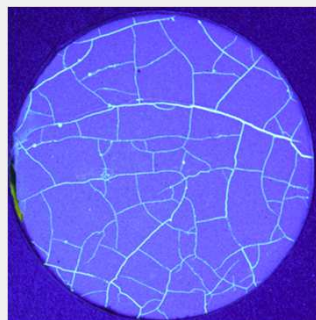
Accelerated carbonation

- ▶ Pastes prepared in **2012** This study
- ▶ CEM V/A with **w/c = 0.40**
- ▶ Disks $\varnothing 50 \times 6$ mm
- ▶ Complete carbonation
- ▶ Accelerated carbonation at 25°C , 55% RH & **3% CO_2**

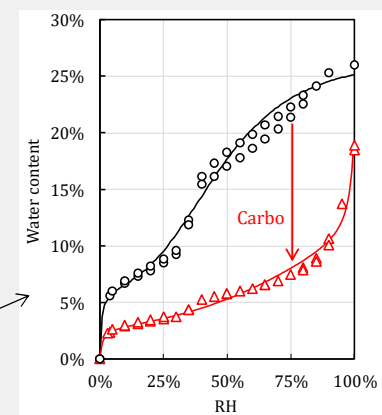
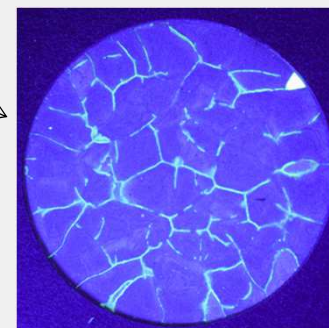




Accelerated carbonation



Natural carbonation



Cracking pattern
after carbonation

In both cases:

- ▶ Significant cracking induced by C-S-H decalcification
- ▶ Similar modifications of the desorption isotherm

Impact of carbonation
on the desorption isotherm

Influence of temperature

- ▶ Decrease of water content when temperature is increased
- ▶ Mainly due to the shift of equilibrium between vapour and adsorbed water
- ▶ Can be described using Clausius-Clapeyron equation
 - isosteric energy of adsorption q_{st}
 - assessment of the influence of temperature on the desorption isotherm
- ▶ **Current work:** methodology for straightforward measurement of q_{st}
 - comparison/validation purposes
 - use for cement-based materials

Influence of carbonation

- ▶ Decrease of water content after carbonation
- ▶ And modifications of the desorption isotherm (for binders with SCMs)
- ▶ No coarsening of the pore-structure detected by MIP but significant cracking induced by carbonation
- ▶ Consequences influence of carbonation = competition between pore-clogging and cracking that depended on the considered binder (SCMs)
- ▶ **Current work:** influence of aggregates (concrete) on changes in transport properties induced by carbonation

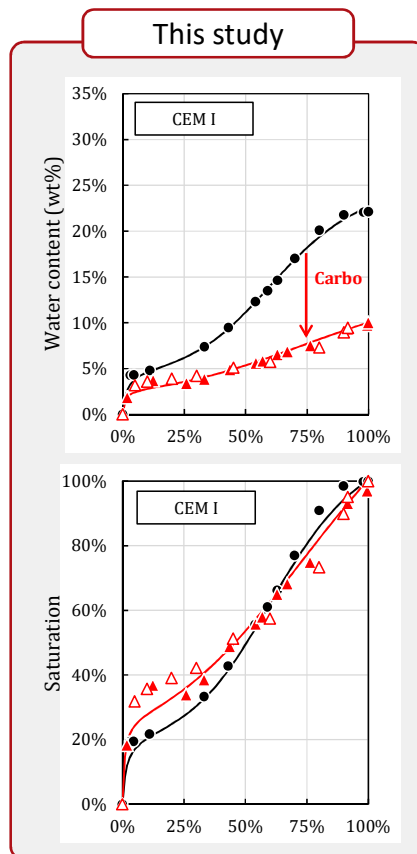


Thanks for your attention

Many thanks to:

- EDF, Andra, CEA for funding
- E. Drouet, M. Auroy, S. Charles, P. Le Bescop, T. Charpentier, J.-M. Torrenti, X. Bourbon, Y. Le Pape, C. Gallé (...)

This study
(2015)
OPC paste w/c = 0.40



Houst (1992)

PhD thesis 1108 (EPFL)
(1992)
OPC paste w/c = 0.40

