



Thermo-mechanical couplings of concrete at early age: from material to structure

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Bron, France

***“From concrete nanoscale to structure”
Celebrating Gilles Chanvillard’s memory***

July 5-6 2016



Ministère
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et de la Mer

Overview

- Back to researches carried out during the 90's at ENTPE
 - → **my PhD [1993 -1998] supervised by Gilles Chanvillard**
- Some additional researches and studies performed at LCPC (now IFSTTAR) and CETU a few years later
- *Good agreement between lessons learned from past experience and the strategic and practical direction set by Lafarge Holcim today*



Training by research ENTPE [1993-1998]

- Each year, about 10 young engineers have the opportunity to do a PhD
- Gilles? A human and a professional story. The feeling to be part of a great “family” that never won’t leave you ... indifferent
 - Gilles, a genius teacher!
 - He was just back from Canada and was teacher/researcher at ENTPE
 - He was really keen on concrete and he fascinated all students with his energy, passion and contagious laugh
 - At that time, everything had to be done regarding concrete research at ENTPE
- I liked construction materials
- I was dreaming to teach and to do researches
- I was fascinated by the well-known play:
« Les Palmes de monsieur Schutz » ...



The short story of the thesis topic



- At the beginning, I'd like to do a PhD on lunar concrete! (I guess, I used to watch too much TV ...)
- Gilles: "C'est génial !"
- A few days later, he had already found documents on lunar concrete: the committee report ACI SP 125 « Lunar concrete » (1991)
- But, we had to land on earth and we understood that we had to behave as "politician" and to find a more consensual subject
- A collaboration was launched between LCPC and ENTPE about concrete strength estimation at early age. In the long term, the main goal was to implement a specific module in the FE program CESAR-LCPC
- Jean Michel TORRENTI supervised the research theme on the mechanical behavior of concrete at LCPC
- And thus began my PhD with all the support I could never have imagined ...

Lunar Concrete



Richard A. Kuhn, Editor - SP 125

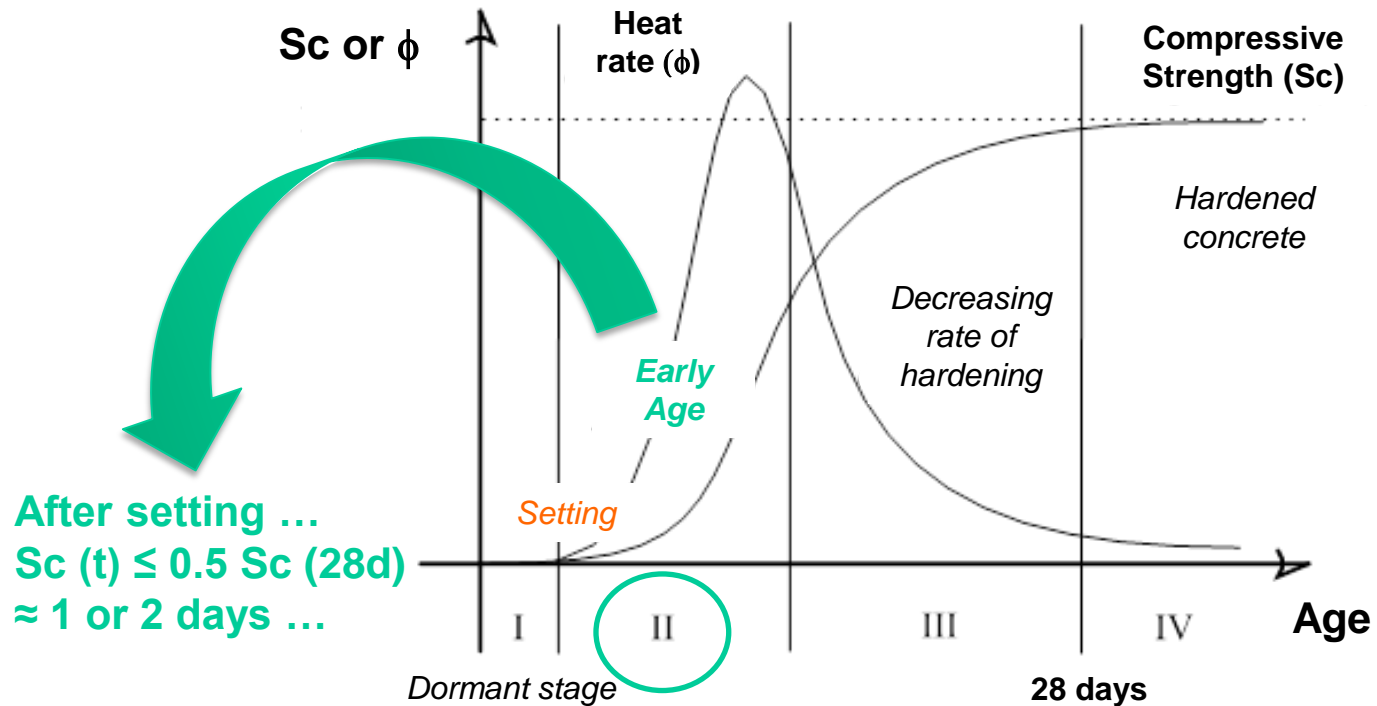


Lunar Base, Shimizu

Concrete at Early Age



Early Age of concrete?



Cement hydration \approx Chemical reactions between cement and water
 \rightarrow concrete hardening and temperature increase within structures

Early age main issues

- **Concrete strength estimation:**

- Small standard samples don't reproduce the actual in-place concrete temperatures → don't represent the actual concrete strength development
 - *How to accurately estimate the in-place concrete strength to ensure formwork removal, early and safe pre-stressing?*

⇒ *Optimization of the rate of building by accounting for thermal effects!*

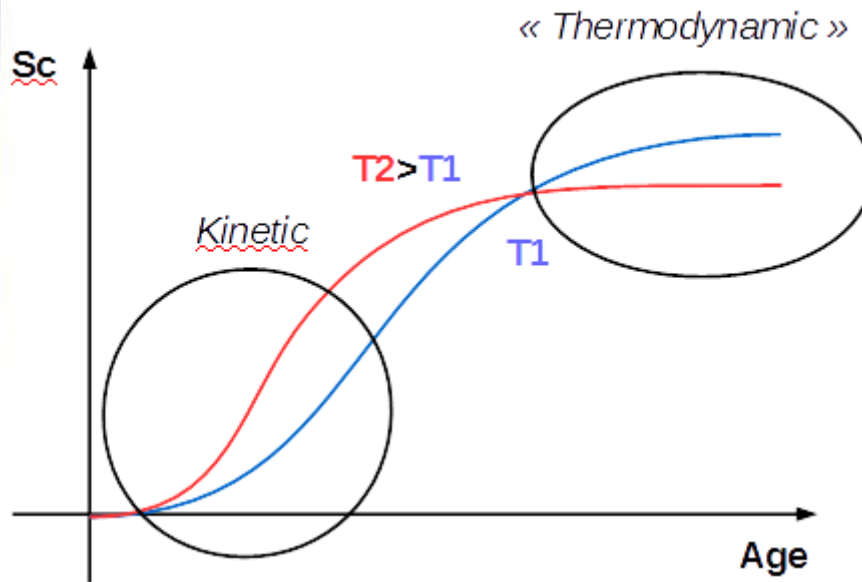
- **Temperature and thermal gradients estimation:**

- Competition between heat released within massive concrete structures and its diffusion to the ambience
 - *How to limit the induced thermal stress to avoid thermal cracking?*
 - *How to avoid high temperature at early age to prevent chemical disorders from appearing?*

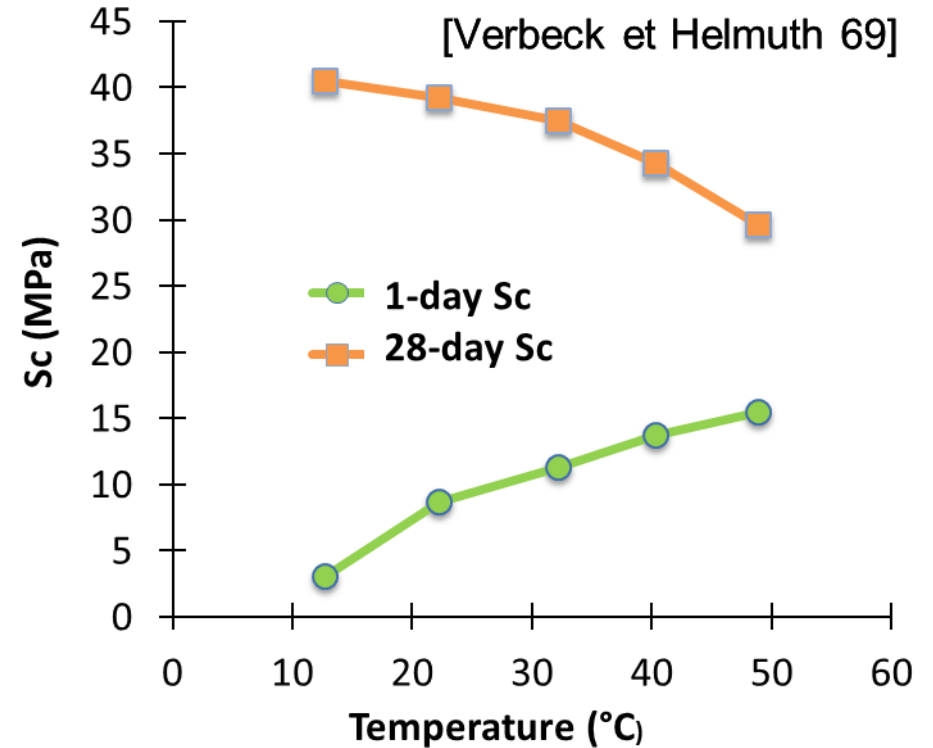
⇒ *Improvement of durability by limiting thermal gradients and high temperature at early age!*

Influence of temperature on concrete strength

Isothermal curing:



[Byfors 80] [Laplante 93] [D'Aloia 93]...



- ➡ Kinetic effect at early age: $\uparrow T \rightarrow \uparrow$ rate of hardening
- ➡ “Thermodynamic” effect at later ages: $\uparrow T \rightarrow \downarrow$ Sc

“Maturity” and the concept of “Equivalent Age”

■ “Maturity”:

- *“Concrete of the same mix at the same maturity has approximately the same strength whatever combination of time and temperature go to make up that maturity”* [Nurse 49] and [Saul 51] [Nikänen 56]

$$M(t, H(T)) = \int_0^t K(T(\tau)) d\tau = M(t_{eq}, T_{ref}) = K(T_{ref}) t_{eq}$$

$M(t, H(T))$: maturity at age t for a given temperature history $H(T)$

$H(T)$: temperature history : $T(\tau), \tau \in [0, t]$

$K(T)$: rate constant,

$T(t)$: temperature, K

■ “Equivalent Age”:

- *“The Equivalent Age represents the age of curing at the reference temperature that would result in the same strength as would result from curing at other temperatures”* [Rastrup 54] [Mac Intosh 56] [Freiesleben Hansen and Pedersen 77]

$$t_{eq} = \int_0^t \frac{K(T(\tau))}{K(T_{ref})} d\tau$$

$M(t_{eq}, T_{ref})$: maturity at age for the reference temperature, T_{ref}

t_{eq} : equivalent age at the reference temperature T_{ref} usually 20° C (293K).

$$t_{eq \text{ FHP}} = \exp\left(-\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right) t$$

Influence of temperature

- **“Kinetic”** effect:

- Arrhenius’ law (“simple” chemical reaction! → approximation in the case of cement hydration) → rate constant expression $K(T)$ and reaction rate (v):

$$K(T) = A \exp\left(-\frac{Ea}{RT}\right)$$

$$v = \frac{\partial \alpha}{\partial t} = K(T)g(\alpha)$$

T : absolute temperature, K

R : gas constant, 8.314 J/mol K

Ea : «Apparent» Activation Energy, J/mol

v : hydration rate

α : hydration degree (Sc/Sc_{final} or q/q_{final})

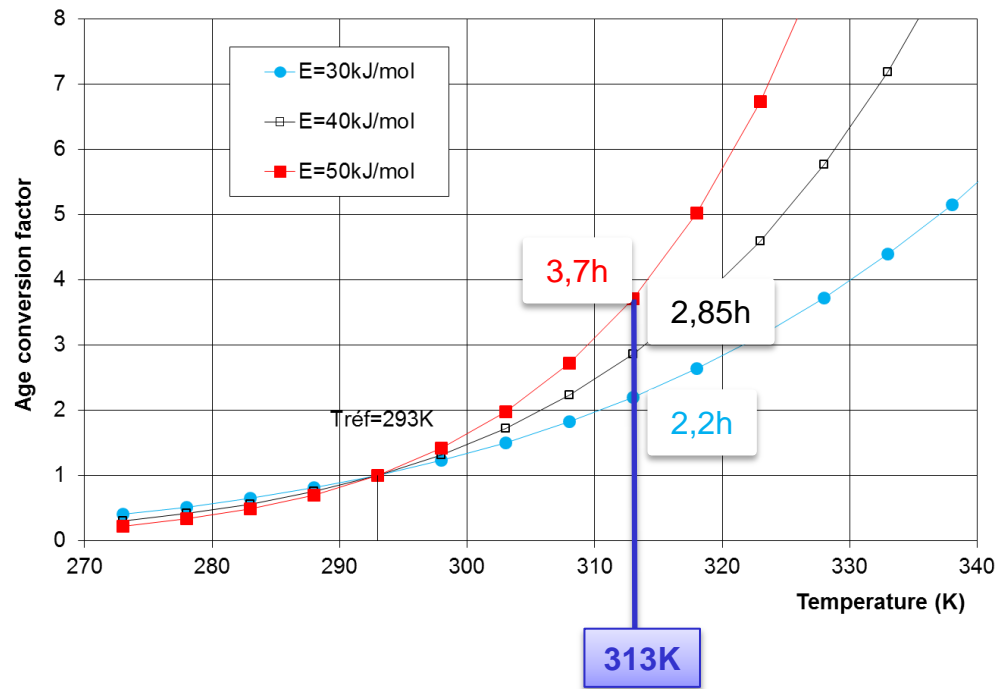
g(.) : function of α



- Ea is the **“apparent”** activation energy of concrete
- Ea can depend on **mix design parameters** (type of cement, w/c, mineral additions, ...) and physical variables: **T and α**
- Ea has to be **experimentally** determined!

γ and E_a

For isothermal curing
 “Age conversion factor”: $\gamma = \frac{t_{eq}}{t} = \frac{K(T)}{K(T_{ref})} \exp\left(-\frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right)$



[D'Aloia 98]

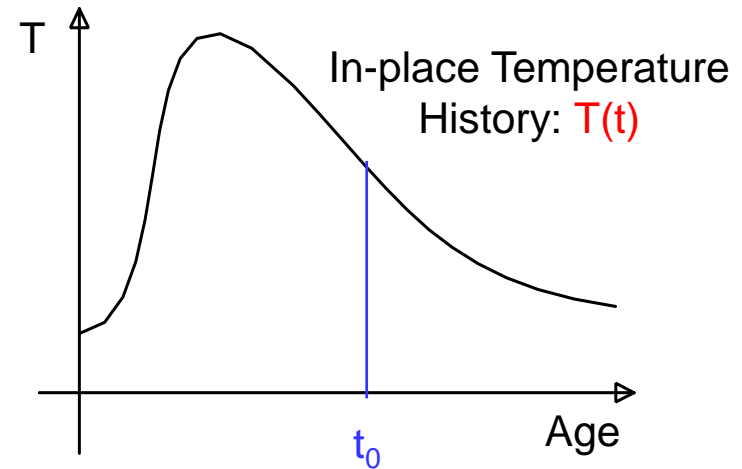
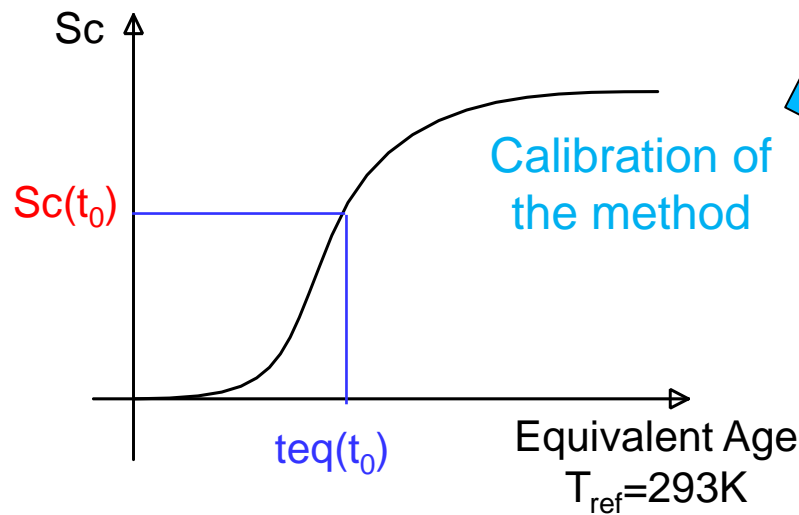


E_a represents the **sensitivity of the hydration kinetic** to a change in temperature

Concrete strength estimation at early age

- Application of the **method of “Equivalent age”** to the estimation of in-place concrete strength:

1) “Reference Curve”: $(Sc, teq) + Ea$

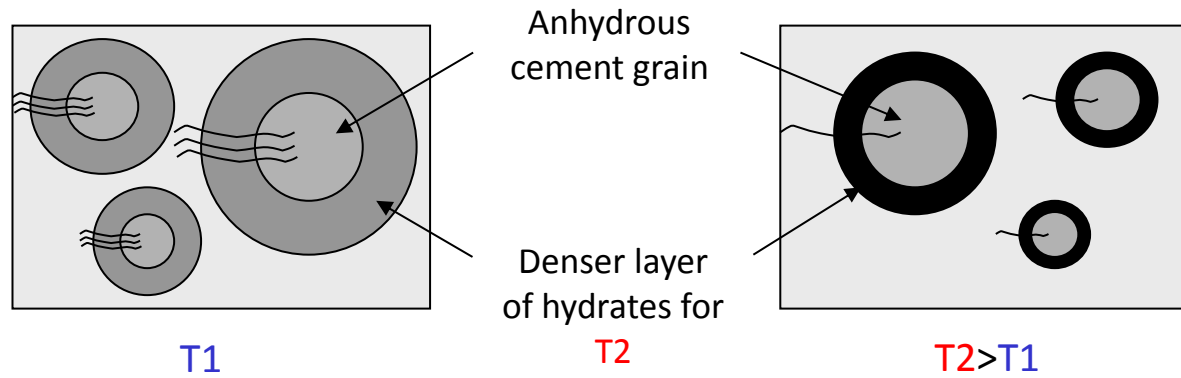


3) Sc(t₀)

$$2) \quad teq(t_0) = \int_0^{t_0} \exp\left(-\frac{Ea}{R} \left(\frac{1}{T(\tau)} - \frac{1}{T_{ref}}\right)\right) d\tau$$

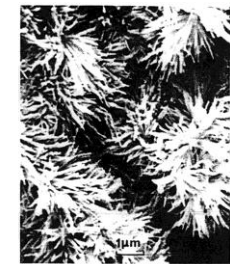
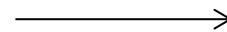
Influence of temperature

- “Thermodynamic” effect:



- A different and more heterogeneous hydrates arrangement and a lower final cement hydration degree at higher isothermal curing temperature

[Verbeck and Helmuth 69]
 [Regourd et Gautier 80]
 [Kjellsen 90] [Van Breugel 91]



C-S-H formation at 20 and 80° C



- A differential thermal expansion of constituents and a setting at high temperature

[Kjellsen 90] [Laplante 93]



Precautionary measure for precast concrete!

Long term compressive strength modelling

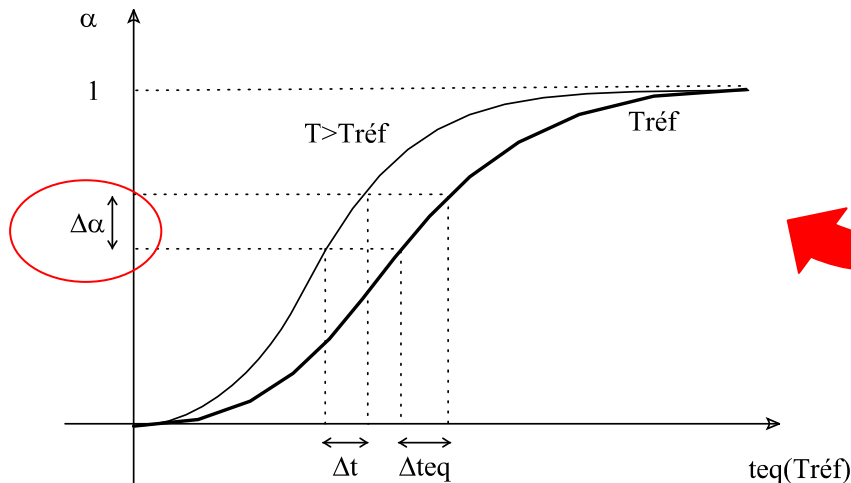
- **First idea:** to improve concrete strength estimation at early age by accounting for the “thermodynamic” influence of T on Sc_{28d}

Isothermal curing: $T \rightarrow Sc_{28d}$

$$Sc_{28d}(T) = Sc_{28d}(293K)(1 - k(T - 293))$$

- On the basis of a literature review (fitting on experimental results): $k = 0.01$
- The method of equivalent age is applied to the estimation of α

$$Sc(t, H(T)) = \sum_t Sc_{28d}(T) \Delta\alpha(\Delta t, T) = \sum_t Sc_{28d}(T) \Delta\alpha(\Delta t_{eq}(T_{réf}))$$



The method was improved ! BUT ...

- Modeling was not really satisfactory ...
- Mathematical model of interpolation
- Setting time
- Proper determination of E_a ?

[Chanvillard D'Aloia 1997]

Ea determination

Type of test and method?



Mechanical or Calorimetric tests?

- Determination of E_a : obtained by comparing at least two different thermal conditions (two tests)

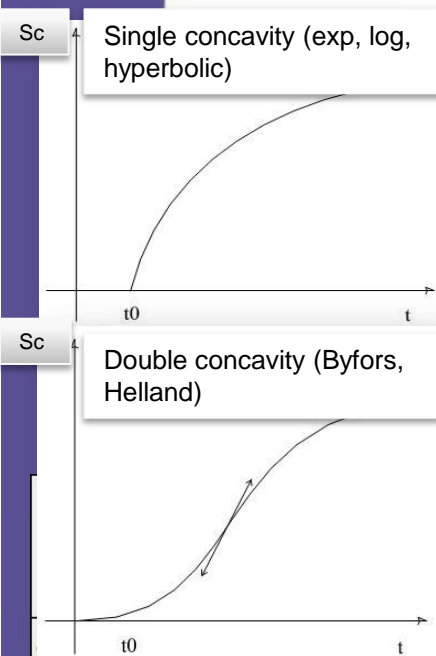
- **Mechanical tests:**

- **Main drawbacks:**

- discontinuity of experimental results and use a model of interpolation
 - strong influence of T on Sc_{28d}
 - test procedure ...

- **Main advantages:**

- same property as that you are supposed to estimate!
 - setting time ...



[Byfors 80]

$$Sc = \frac{at^b}{1+ct^d}$$

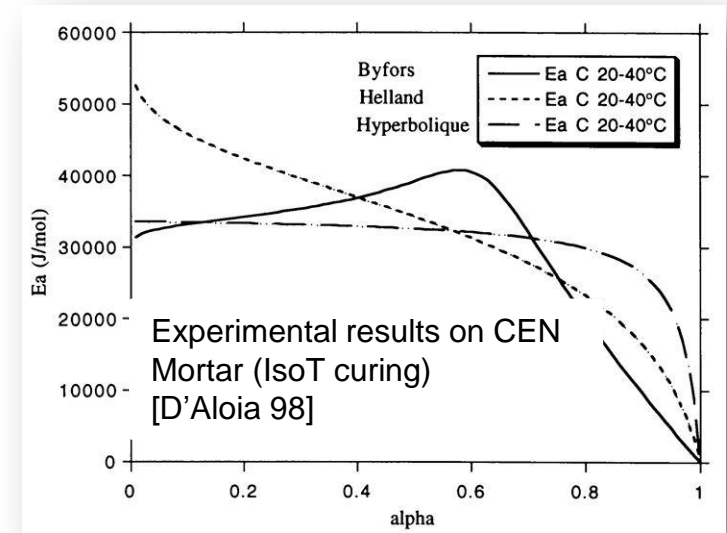
[Helland] ...

$$Sc = Sc_{\infty} \exp\left(-\left(\frac{b}{t}\right)^c\right)$$

[McIntosh 56]
[Carino 82]...

$$Sc = \frac{t-t_0}{\frac{1}{A} + \frac{t-t_0}{Sc_{\infty}}}$$

with t_0 setting time



Strong dependence of E_a on the mathematical model of interpolation

Mechanical or Calorimetric tests?

- **Determination of E_a : obtained by comparing at least two different thermal conditions (two tests)**
 - **Calorimetric tests** (2 different thermal conditions):
 - **Main advantages:**
 - continuous measurement
 - easier test procedure
 - no significant influence of T on q_∞ or q_{28d}
 - **Main drawback:**
 - additional step of mechanical validation
 - **3 types** of calorimetric tests:
 - **Adiabatic** (“CERILH” calorimeters)
 - **Semi adiabatic** (LCPC-QAB calorimeters for concrete and Langavant calorimeters for mortar (NF EN 196-9))
 - **Isothermal** ...



The choice of the type of test could depend on expected temperatures



Calorimetric tests

- **Semi-adiabatic calorimetry:** thermal exchanges with the ambience → **LCPC-QAB calorimeters** (“quasi-adiabatic”) for concrete and **Langavant** (NF EN 196-9)) for mortar



- Thermal losses are calculated :
 - Calibration of QAB calorimeters :
 - coefficients of thermal losses have to be experimentally determined: a et b
 - specific heat of the calorimeter: μ

- A control calorimeter is required (inert specimen)

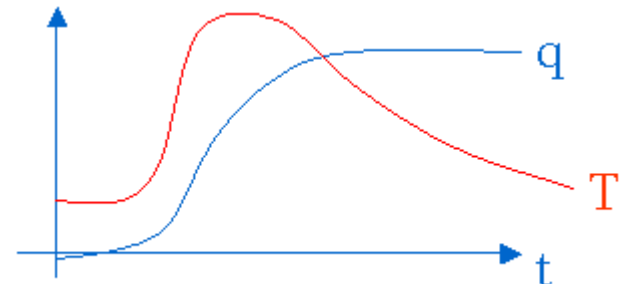
$$\theta(t) = T(t) - T_{control}(t)$$

- The ambience needs to be regulated $T_{ambient} \approx T(t_0) \approx T_{control}$

Calculation of hydration heat

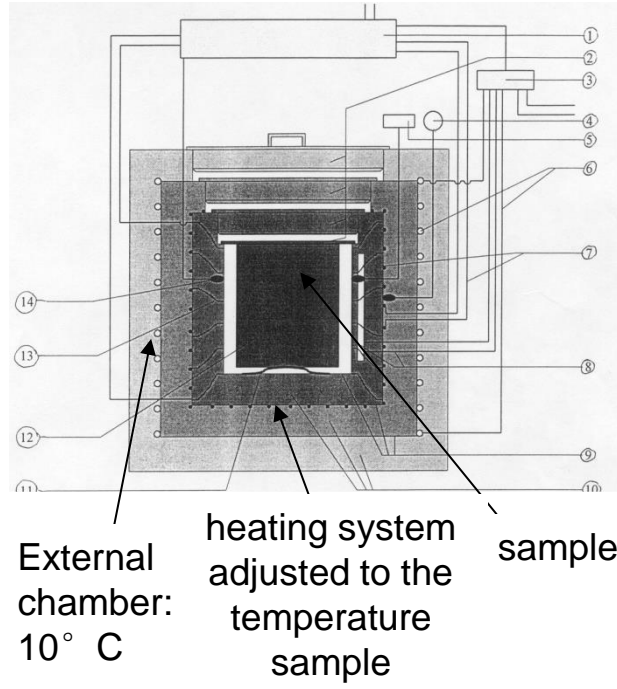
$$q(t) = \frac{C}{m_c} (\theta(t) - \theta_0) + P(t)$$

$$= \frac{C}{m_c} (\theta(t) - \theta_0) + \frac{1}{m_c} \int_0^t (a\theta(\tau) + b\theta^2(\tau)) d\tau$$



Calorimetric tests

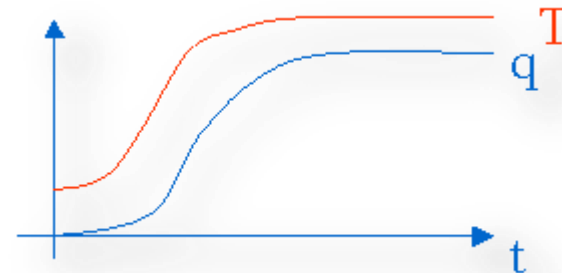
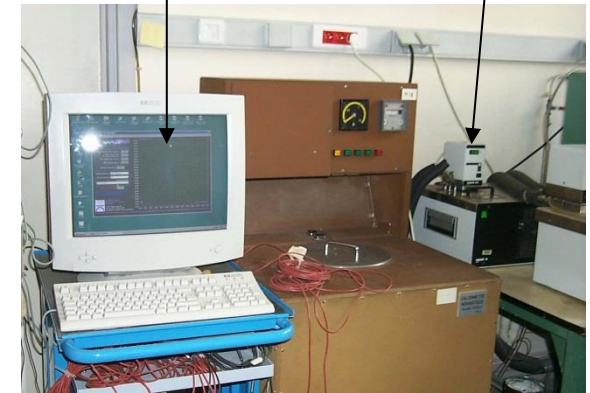
- **Adiabatic calorimetry:** no thermal exchange with the ambience OR the ambient temperature is adjusted to the core temperature of the sample → **"CERILH" calorimeters** for concrete
 - Calibration of calorimeters :
 - Specific heat capacity of the calorimeter: μ
 - The ambience doesn't need to be regulated



Calculation of hydration heat

$$q(t) = \frac{C}{m_c} (T(t) - T_0)$$

Recording device cryostat



Ea Estimation?

- Ea is determined on the basis of two calorimetric tests initiated at two different temperatures
- Two analyzing methods:
 - The “**superposition method**”
 - The “**speed method**”

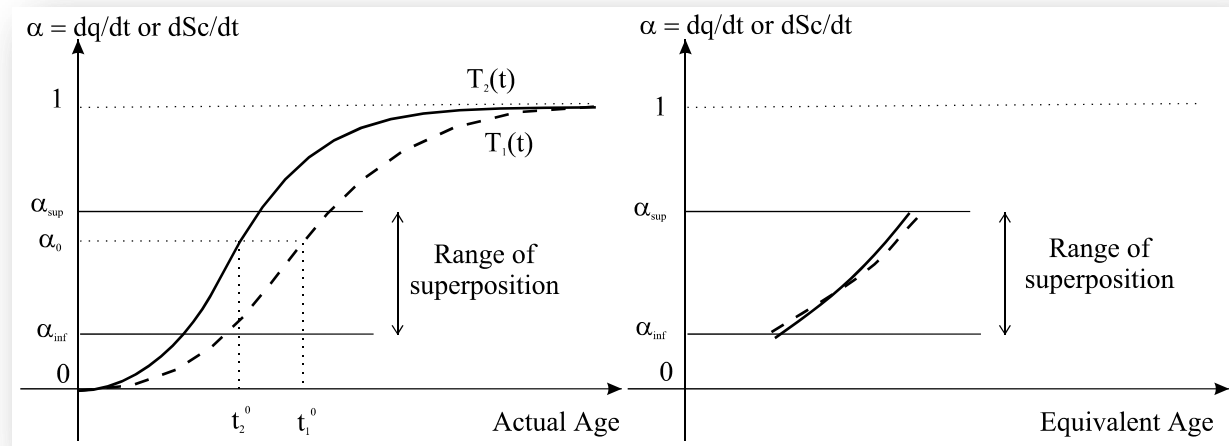


Ea Estimation?

- Ea is determined on the basis of two calorimetric tests initiated at two different temperatures
- Two analyzing methods:
 - The “**superposition method**” → for calorimetric or strength tests

a least squares criterion:

$$\min_{Ea} \left(\sum_{\alpha_i \in [\alpha_{inf}, \alpha_{sup}]} |t_{eq1i} - t_{eq2i}|^2 \right)$$



$$t_{eq1i} - t_{eq2i} = \int_0^{t_{1i}} \exp\left(-\frac{E_a}{R} \left(\frac{1}{T_1(\tau)} - \frac{1}{T_{ref}}\right)\right) d\tau - \int_0^{t_{2i}} \exp\left(-\frac{E_a}{R} \left(\frac{1}{T_2(\tau)} - \frac{1}{T_{ref}}\right)\right) d\tau$$



Several distinct Ea-values can be determined. The concept of "doublet" or "triplet" (2 or 3 Ea-values) was proposed by the CTG Italcementi. Each Ea-value can be adopted depending on the extent of hydration [Roussel 1996]

Ea Estimation?

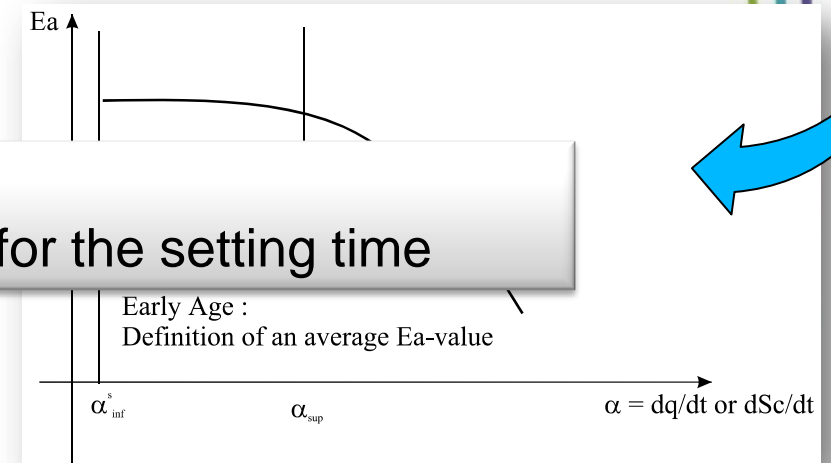
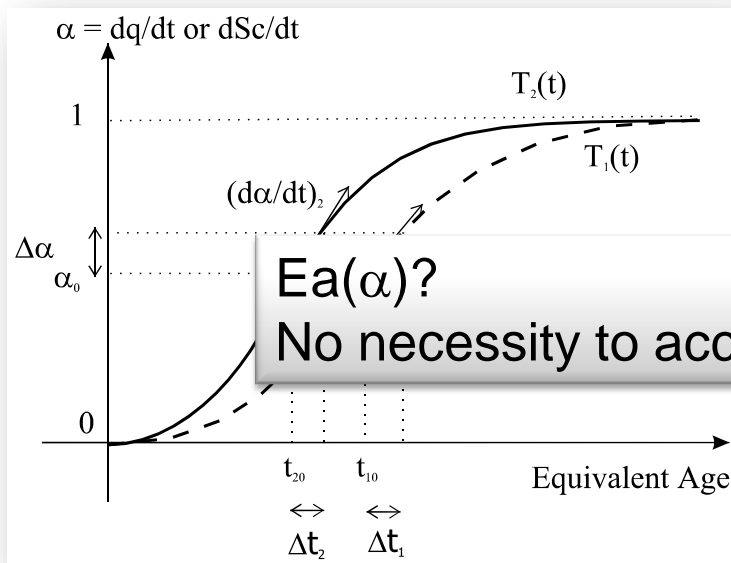
- Ea is determined on the basis of two calorimetric tests initiated at two different temperatures
- Two analyzing methods:

- The “speed method”

$$\frac{d\alpha}{dt} = f(\alpha) \exp\left(-\frac{E_a}{RT}\right)$$

$$\left(\frac{d\alpha}{dt}\right)_1(\alpha_0) = \left(\frac{d\alpha}{dt}\right)_2(\alpha_0) \exp\left(-\frac{E_a}{R} \left(\frac{1}{T_1(\alpha_0)} - \frac{1}{T_2(\alpha_0)}\right)\right)$$

$$E_a(\alpha_0) = -\frac{R}{\frac{1}{T_1(\alpha_0)} - \frac{1}{T_2(\alpha_0)}} \ln \frac{\left(\frac{d\alpha}{dt}\right)_1(\alpha_0)}{\left(\frac{d\alpha}{dt}\right)_2(\alpha_0)}$$





Experimental campaigns



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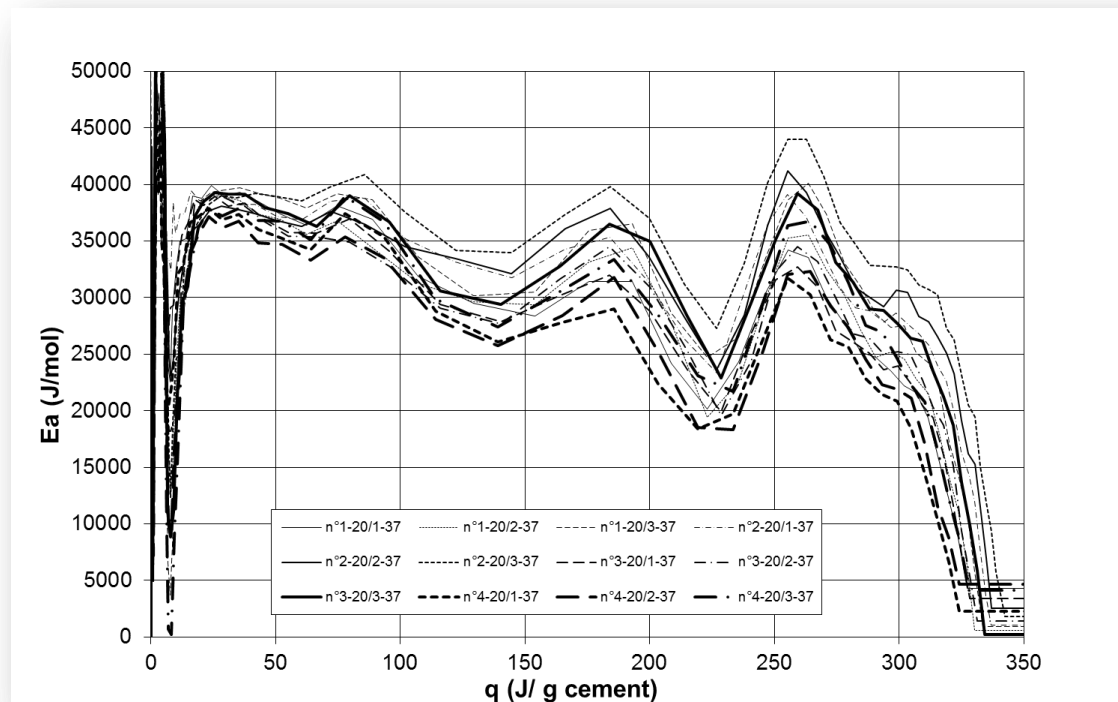
Experimental campaigns

- Most of these campaigns have been performed in collaboration with the CTG - Italcementi Group (Pierre LAPLANTE, Sylvie LECRUX, Vincent WALLER) and with the CETE de Lyon (Sylvie ARNAUD) → French National Project CALIBE (Quality of concrete)
 - Calorimetric and mechanical campaigns
 - Wide range of initial temperatures: [10, 37° C]
 - Concrete and equivalent mortars
 - Different types of cement: CEMI, CEMII, CEMIII (different C3A contents – mineral additions and SP - ...) → Sensitivity of the setting time and E_a to temperature?
 - The test procedure for semi-adiabatic calorimetry has been more detailed to prevent results from being distorted by experimental errors
 - ...

- *Some lessons drawn from experimental campaigns ...*

Repeatability

- Langavant (mortar) – CEMI 52,5:
 - 4 tests at $T_{ini}=20^{\circ}$ C and 3 tests at $T_{ini}=37^{\circ}$ C
 - E_a has been calculated from 10 to 25 and 40% of hydration (**Discrepancies were limited: $E_a \rightarrow 5\text{kJ/Mol}$**)





Numerical modeling



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Numerical simulations

Hydration heat modeling

- **The idea at the basis of the modeling:**
 - To simulate heat rates under adiabatic conditions for different initial temperatures to determine E_a
 - « Apparent » activation energy $E_a \rightarrow$ **multi phasic approach: E_{a_i} for each i-phase**
 - **Main assumption:** independent hydration rates of cement phases ($\approx 24h!$) \rightarrow cement hydration rate
 - Thermal coupling are accounted for (**Arhenius' Law**)
 - Microstructural effects are neglected (fineness, particle size distribution, ...)

[D'Aloia Chanvillard 2002]

Hydration heat modeling

- Data:**

- Cement:** mineral composition (Bogue's formula) including SO_3

- For each cement phase: \rightarrow

$$Ea^i, \left(\frac{dq^i}{dt} \right)_{T_{\text{réf}}} (q^i), q_{\text{max}}^i$$

- Existing data:** [Kishi Maekawa et al. 95] ...
[Parrott et Killoh 84] ...

- Kinetic model** and fitting of parameters

Avrami-Erofeev, [Banfill 94] ("ciments fondus")

$$\alpha^i(t) = 1 - \exp(-K_i t^{n_i})$$

n_i, K_i parameters

$20 < Ea^i < 70$ kJ/mol

$K_i > 0$

$2 \leq n_i = n_{i,\text{nucleation}} + n_{i,\text{growth}} \leq 6$

- Experimental campaign: **calorimetric results**

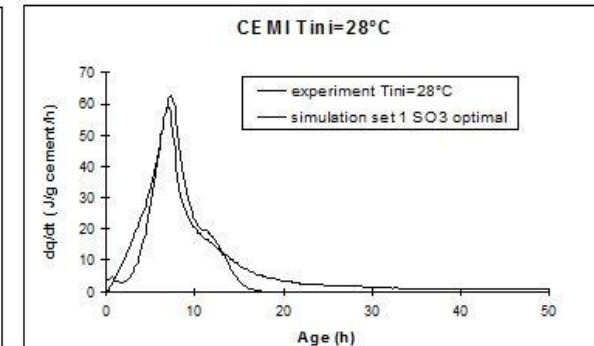
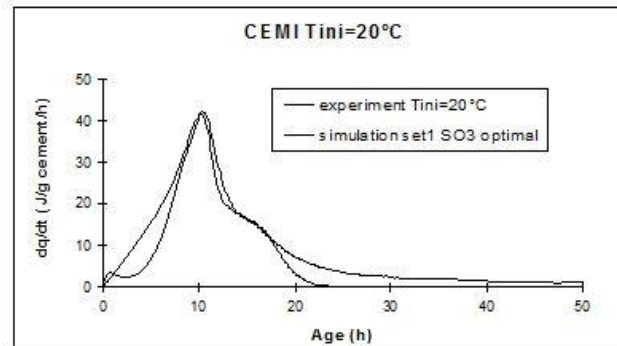
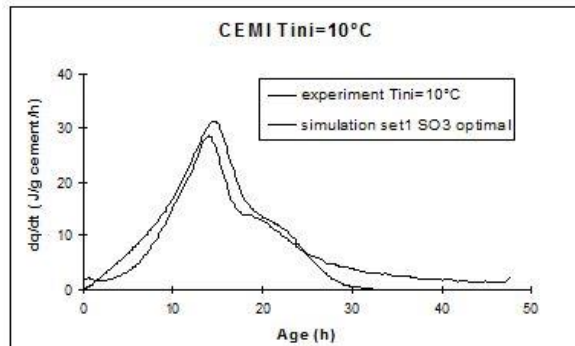
(%)	CEMI	PMES
C_3S	47.66	53.63
C_2S	24.89	21.83
C_3A	9.52	3.04
C_4AF	7.14	12.31
SO_3	3.55	2.86

Hydration heat modeling

- **Constraints and fitting:**

$$\text{C}_3\text{A} + \text{SO}_3 \xrightarrow{\alpha_0} \text{Ettringite} \xrightarrow{\alpha_0 = 0.9} \text{monosulfoaluminate}$$
 - **set 1 and set 2 (C3S and C3A):**
 - Heat rate peak of C3A precedes that of C3S
 - Optimal SO3 content → conversion into monosulfoaluminate is complete when sulphate is exhausted

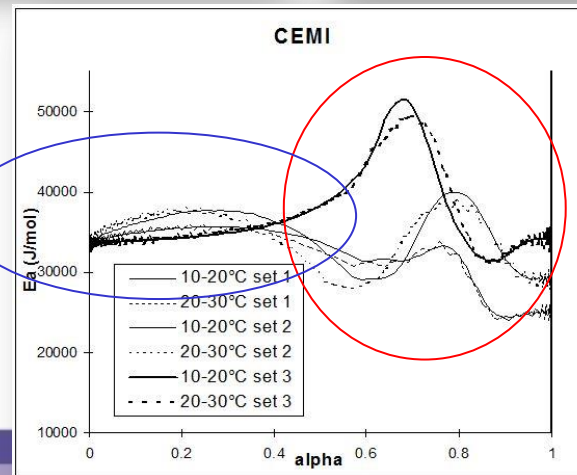
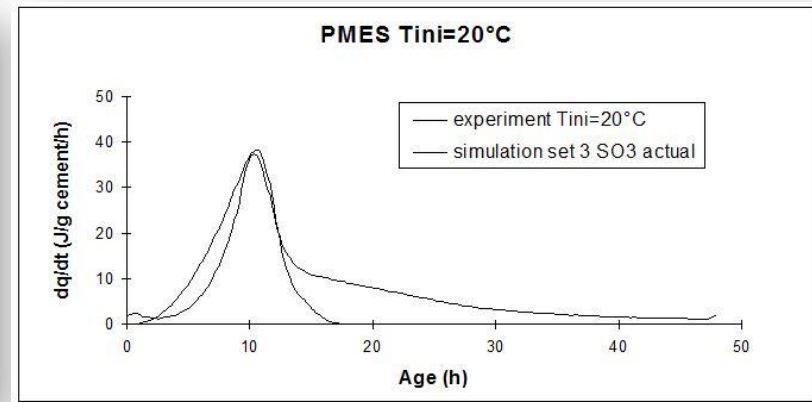
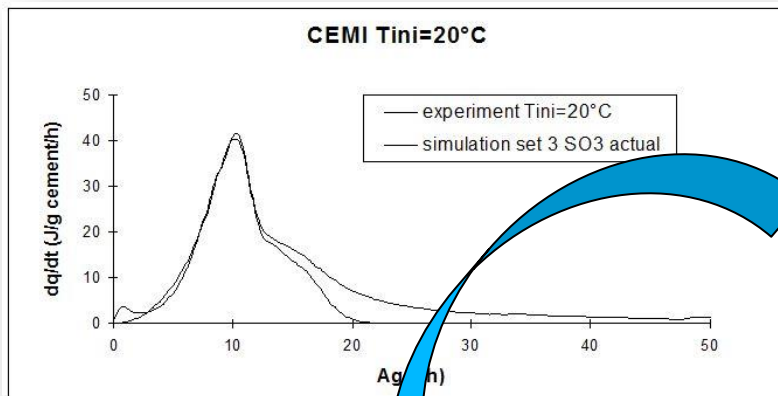
	C ₃ S		C ₃ A → ettringite		ettringite → monosulfoaluminate	
	Set 1	Set 2	Set 1	Set 2	Set 1	Set 2
$K_i (1/t^{n_i})$	5.4^E-3	5.5^E-3	4.7^E-4	4.7^E-4	4.8^E-3	3.5^E-3
n_i	2	2	3	3	2	2
q_{\max}^i *(J/gC ₃ S or C ₃ A)	502	502	1420	1402	1300	1300
Ea^i / R (1/K)	4000	4000	4700	5200	3000	3500



Hydration heat modeling

- **Fitting parameters Set 3:**

- The first peak of C3A (ettringite formation) closely follows the C3S peak
- The two C3A reactions are synchronised at a higher degree $\alpha_0 = 0.4$
- Actual SO3 content

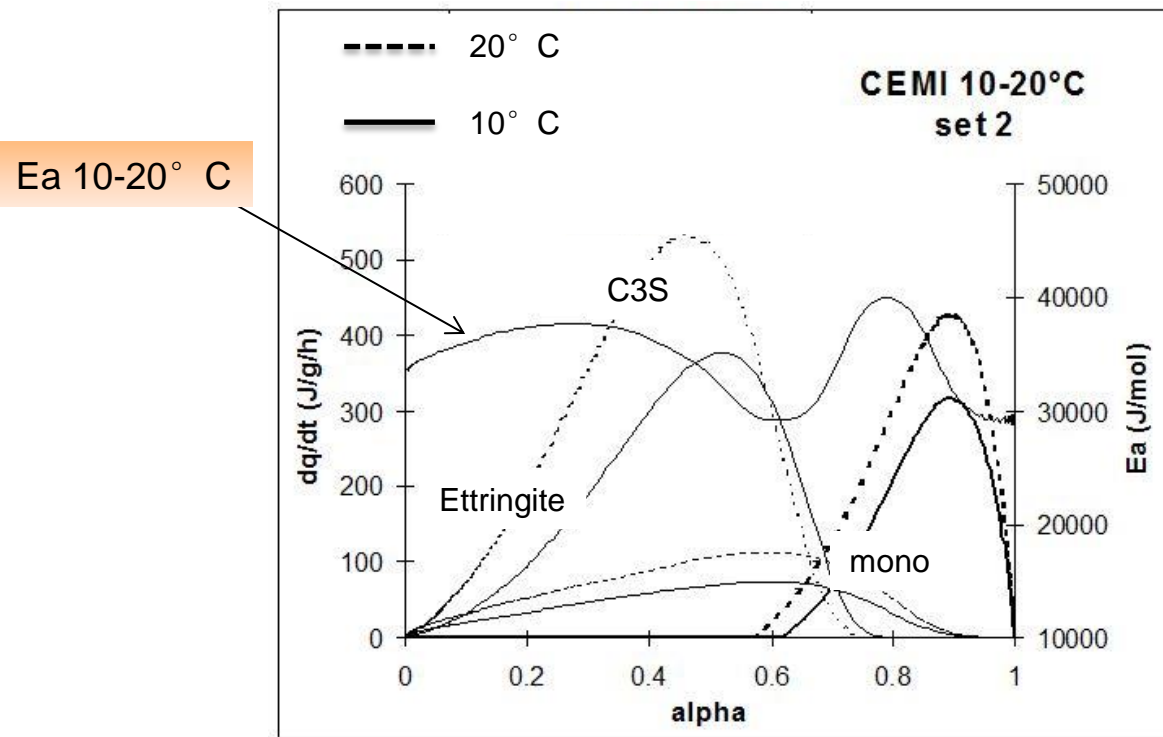


Almost constant and independent of cement
 (→ C3S)

Great variations

Hydration heat simulations

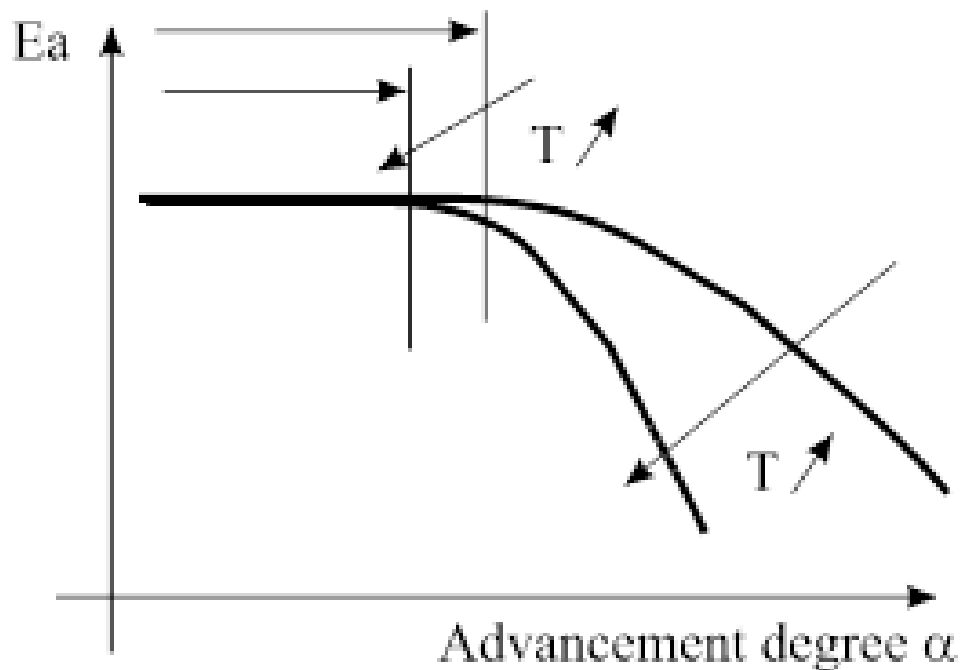
- Parallel evolution of EA and heat flow of phases (CEMI – Set2):



The simulation program CHAL does emphasize the “apparent” nature and the polymineral characteristic of cement

General conclusion on E_a

Plateau at early age :
Calculation of an average E_a -value



Decrease of E_a :
The higher the temperature,
the stronger the slope and
the shorter the plateau



Field applications

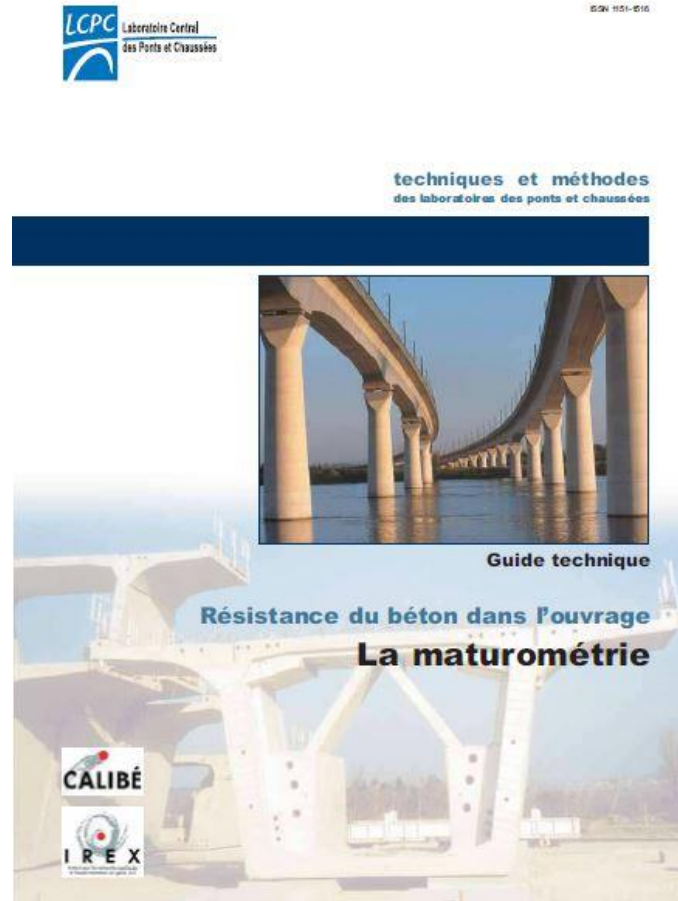


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Concrete strength estimation



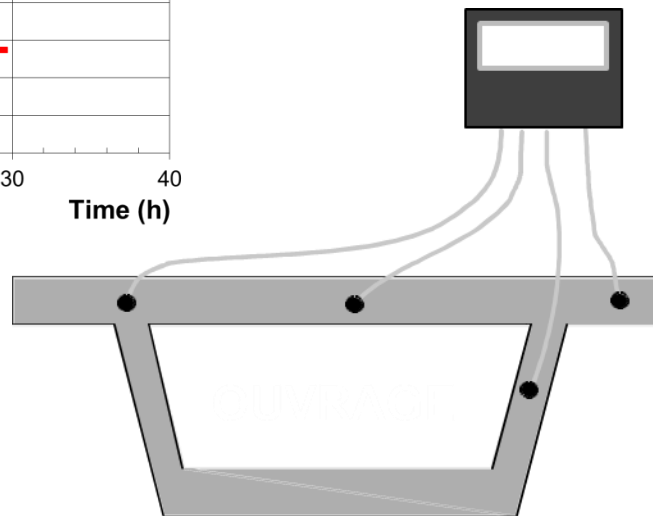
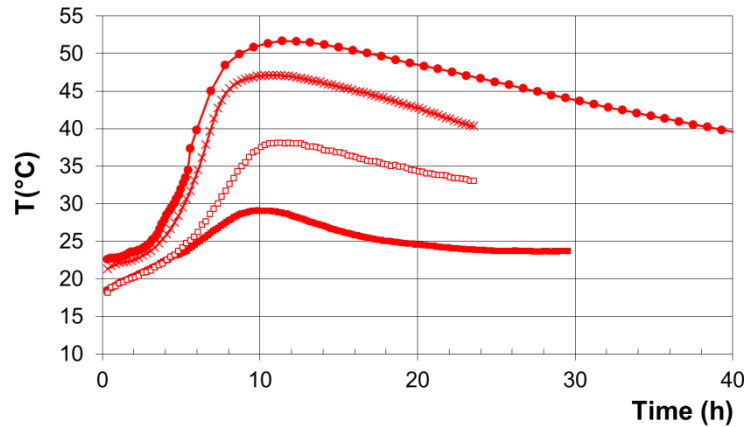
LCPC Recommendations:

“Résistance du béton dans l'ouvrage : La maturométrie”

[Projet National CALIBÉ, 2003]

Concrete strength estimation

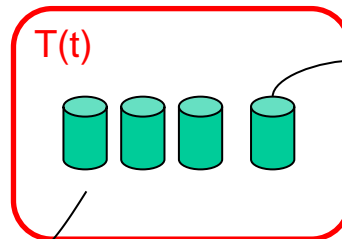
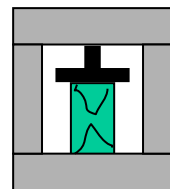
- **Measurement of in-place concrete temperature $T(t)$:**
 - Recording of in-place temperature measurements
 - Calibration parameters are stored in the device
 - Early age concrete strength can be estimated for each thermal history



Concrete strength estimation

- **Calibration of the method: calibration curve and E_a**
 - Thermal conditions of calibration similar to those expected on site!
- **Conformity controls:**
 - Comparison between **measurement** and **estimation of S_c** :
 - Concrete samples are submitted to a given thermal treatment
 - S_c is estimated on the basis of measured temperatures
 - S_c is measured on concrete samples
 - 2 types of conformity controls: at the beginning and during works
- **Main objectives:**
 - To validate the calibration of the method of equivalent age → **reference curve**
 - To control the regularity of process of concrete production

S_c is measured
on concrete samples



S_c is estimated
from temperature
histories



Concrete strength estimation

Field application

- **From the practical point of view** : the superposition method is mostly used on mechanical tests for the calibration of E_a
 - Why? To avoid the additional step of mechanical validation when performing calorimetric tests. Easier tests on site!
 - **Attention should be paid to the calibration procedure!**
- **At an upstream stage (optimization of building phases)** → use of numerical tools. Both the superposition and the speed methods are used for calorimetric tests
 - Easier tests on lab! Several numerical tools ...
- *The maturity method or equivalent age method is often used in France (especially in tunnels...). Last tunnel : Saint B at*





After my PhD



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RÉPUBLIQUE FRANÇAISE



Ministère
de l'Environnement,
de l'Énergie
et de la Mer

Later studies at LCPC - CETU

- **Guide-LCPC “Maturométrie”** (National Project CALIBE) (2003)
- **Calorimetric tests procedures** have been improved, data recording and results analysis automatized for both **semi-adiabatic and adiabatic tests**
- **Calorimetric tests and numerical simulations** performed for specific construction sites and with different goals
 - Viaduct of Verrières (→ Millau bridge) – Concrete mix design and **optimization of phasing ...**
 - **Durability:** evaluation of maximum temperature at early age (DEF)
 - Application to **Self Compacting Concrete (SCC)**
 - **Comparison between adiabatic and QAB tests** (equivalent mortars and concrete)
 - Accounting for **the setting time** in the determination of E_a
 - Accounting for **evaporation** in the estimation of early age temperature by FE Program
 - Better understanding the **cracking of concrete tunnel lining**



Several phenomena have to be accounted for in case of field application! (autogeneous shrinkage, thermal shrinkage, drying ...)

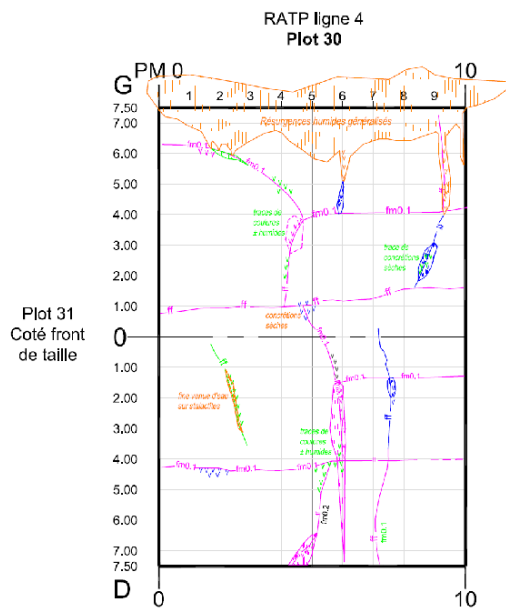
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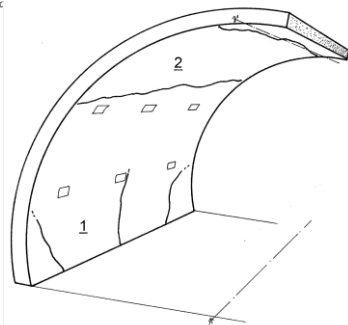
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Other researches CETU – ENS Cachan



- Légende -
- Suivi de la fissuration par couleur suivant l'âge du plot bétonné -

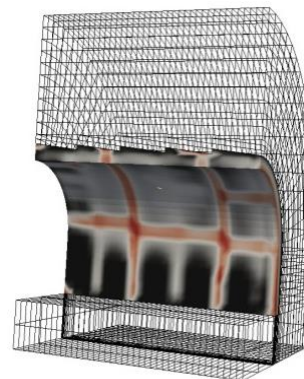
- fissure 0.1 mm (ff = filiforme)
- Zone humide
- Inspection 1 : 29-09-2010 (1 mois)
- Inspection 2 : 26-10-2010 (2 mois)
- Inspection 3 : 25-11-2010 (3 mois)
- Inspection 4 : 02-03-2011 (6 mois)
- Inspection 5 : 24-06-2011 (9 mois)



Influence of micro and macro PP and Metallic fibers on the concrete sensitivity to cracking

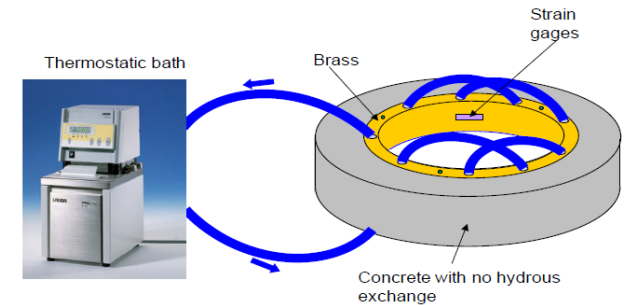
(Subway M4/RATP → replacement of steel mesh – Thick concrete lining without watertightness)

Thermal – Autogeneous and drying shrinkages

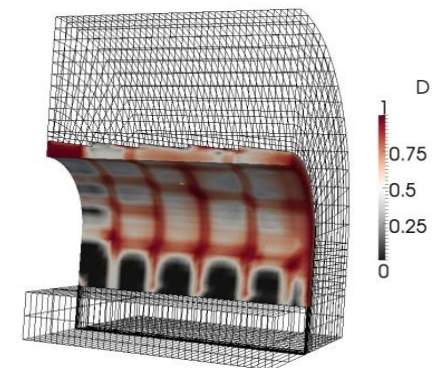


Damage field due to both thermal and autogenous shrinkages after 360 hours (CASTEM)

← including creep



Thermal active ring test



[Briffaut, Benboudjema, D'Aloia 16]



Thank you for your attention
Thank you Gilles!



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