Modelling of concrete/clay interaction :

taking into account complex mineralogy influence of non-saturated conditions and temperature effects

F. Claret, A. Burnol, S. Gaboreau, N. Marty, C.Tournassat, P.Blanc, EC. Gaucher

BRGM, Orléans

With the partnership of:

Andra: X. Bourbon, S. Dewonck, I. Munier, N. Michau

ANDRA

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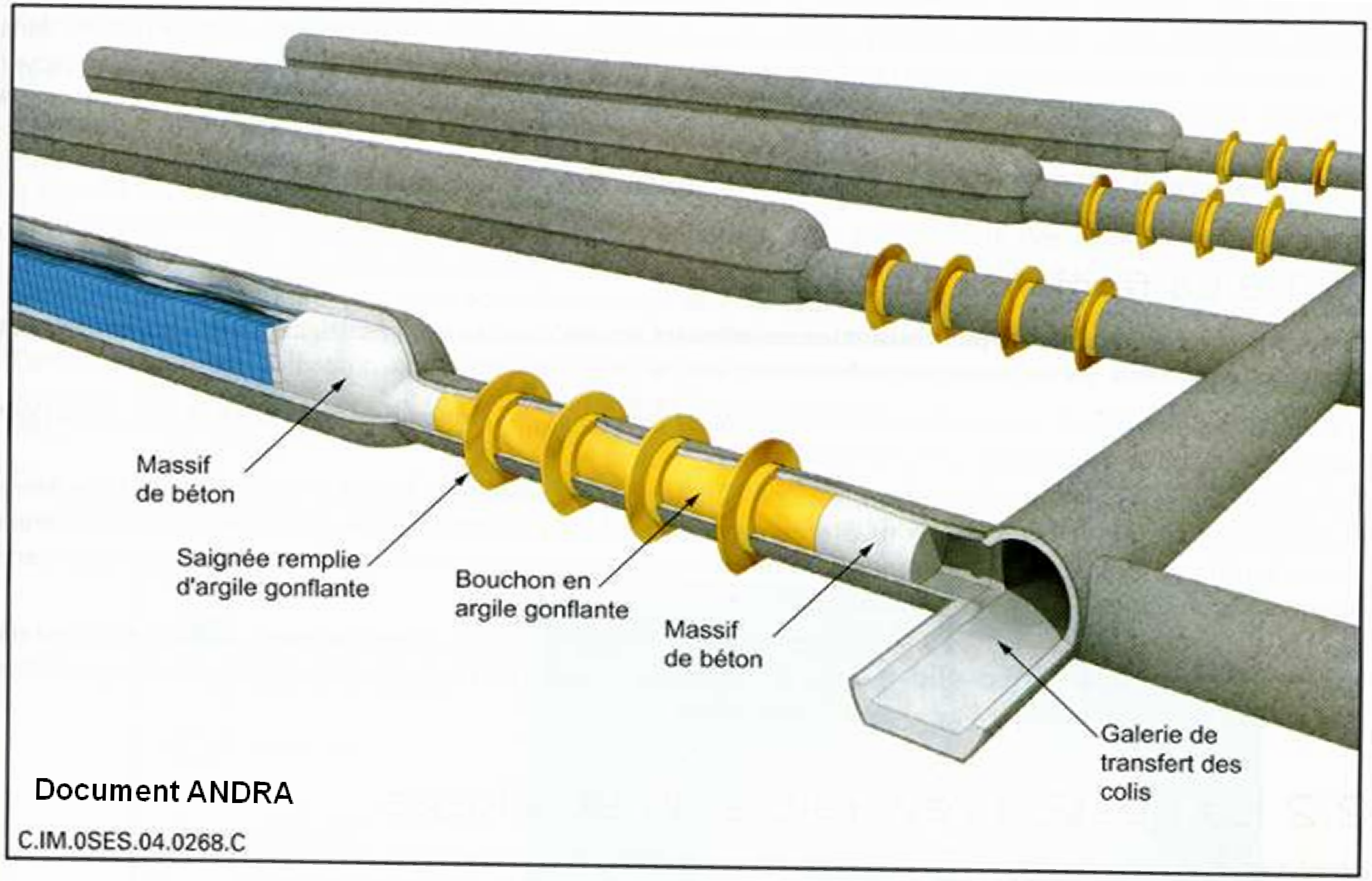
CONTEXT: COX/CONCRETE/BENTONITE INTERACTION



Alvéoles de stockage de déchets B scellées

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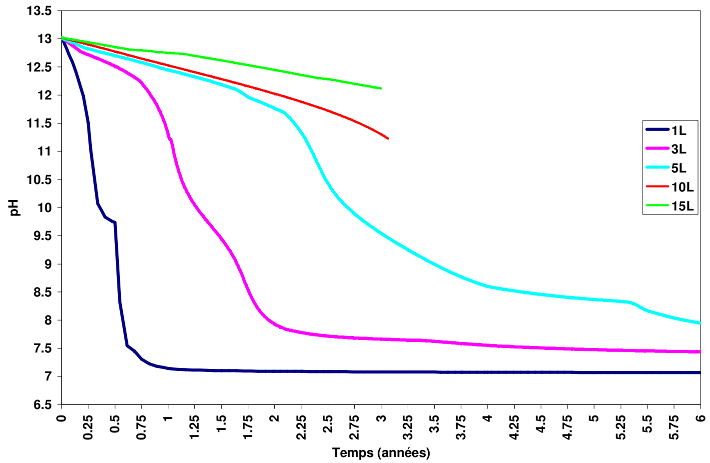
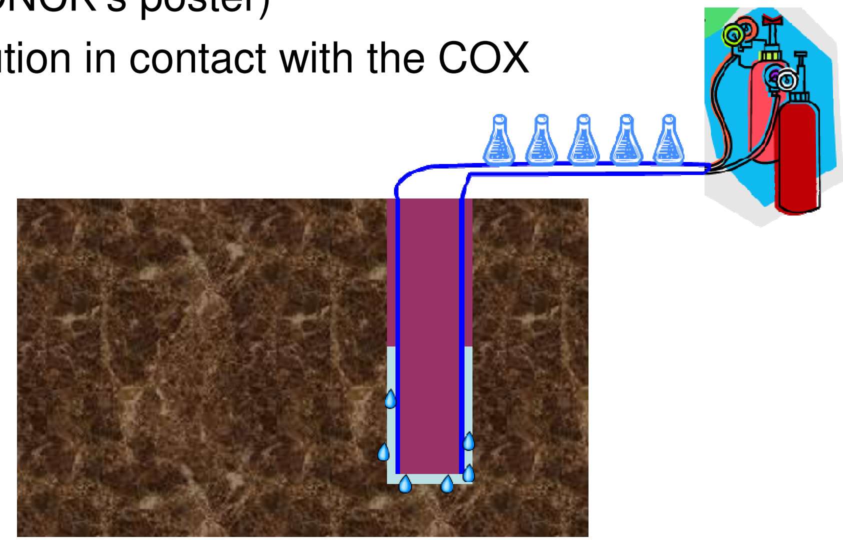
MODELLING AS A TOOL

> To size a future underground experiment in the Bure's Laboratory

- MLH experiment (see S.DEWONCK's poster)
- pH evolution of an alkaline solution in contact with the COX





> To make some predictive calculations

- Long term modelling of concrete/clay interactions for PA purposes

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CRITICAL ELEMENTS FOR THE MODELLING

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- **Transport parameters (porosities, permeabilities, diffusion coefficients, heat conductivities…)**

- **A Transport reactive code**
  - PHREEQC (1D)
  - TOUGHREACT (radial geometry, non saturated condition, ….)
- **Experiments to test and improve the modelling**
- **….**

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http://thermoddem.brgm.fr/

Thermoddem - Mozilla Firefox

Fichier Édition Affichage Historique Marque-pages Outils ?

http://thermoddem.brgm.fr/fiche.asp

Les plus visités | Club Internet | Hotmail | Mon Assistance | Mon compte | Personnaliser les liens | http://www.skitour.fr... | Windows Media | Accès web saturé : po... | Page d'accueil de Mozi... | Page d'accueil de Mozi...

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THERMODDEM

Thermodynamics database devoted to the modelling of waste minerals alteration

- Introduction
- Links and addresses
- Rights of user
- Data consultation

- Help
- Home page
- Login
- More info...

Mineral

Export file (text format)

Nomenclature

Name of mineral : Foshagite
Formula : Ca4Si3O9(OH)2:0.5H2O
family : Inosilicates, Wollastonite-2M - Foshagite series
Other members : Hillebrandite (Ca2SiO3(OH)2:0.17H2O); Wollastonite (CaSiO3)
Polymorphs : No polymorph...

Mineralogy

Space group : Monoclinic - Prismatic H-M Symbol (2/m) Space Group: P 21/m
Dana class : 65.2.2.1 (65) Inosilicate Single-Width Unbranched Chains, W=1(65.2) with chains P=3 (65.2.2) Dana Group

Occurence & geological context

Metamorphosed limestone.

Alteration & pathway

Confined medium :
Weathering :

Thermodynamics

Properties of formation from the elements

$\Delta G°_f$: −5 643 832 J/mol Ref. Info — **Mol wt:** 431.5870 g/mol

$\Delta H°_f$: −6 032 430 J/mol Ref. Info — **V :** 160.6600 cm^3/mol Ref. Info

S°: 295.07 J/mol K Ref. Info

Stability range: High temperature mineral.

Test (consitency): 2 D

Cp Information

Reaction properties: Ca4Si3O9(OH)2:0.5H2O + 8H+ + 0.5H2O = 4Ca++ + 3H4SiO4

Van t'Hoff

Log K: 65.96 Ref. Info — $\Delta H°_r$: −380 238 J/mol Ref. Info

Analytic

$\text{Log K} = A + BT + CT^{-1} + D\,\text{LogT} + ET^{2}$

A : −1 116.01
B : −0.17
C : 78 338.50
D : 405.82

T (°C)	0	25	60	100
	150	200	250	300
	72.08	65.96	59.01	52.75

Terminé

démarrer | Microsoft ActiveS... | Club Internet | Boîte de réception... | iTunes | Thermoddem - Mo... | FR | 09:26

AMORPHOUS CSH

> **Among the various models published that take into account the solubility of CSH, two main families may be distinguished:**
- Discrete phases
- Solid solutions

> **Nowdays integration of solid solutions in transport geochemical codes lead to crippling computing times**

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COMPOSITION OF AMORPHOUS CSH PHASES (1/4)

> **According to the literature and given the crystallographic constraints a 3-phases model was chosen**

> **Such model already exist (CSH0.8/1.1/1.8)**

- Stronach and Glasser (1997) Adv. Cem. Res. Vol. 36 pp.167
- A.C. Courault (2000) Thesis Université de Bourgogne

> **Strategy used : fitting of the literatures data with a least squares algorithm**

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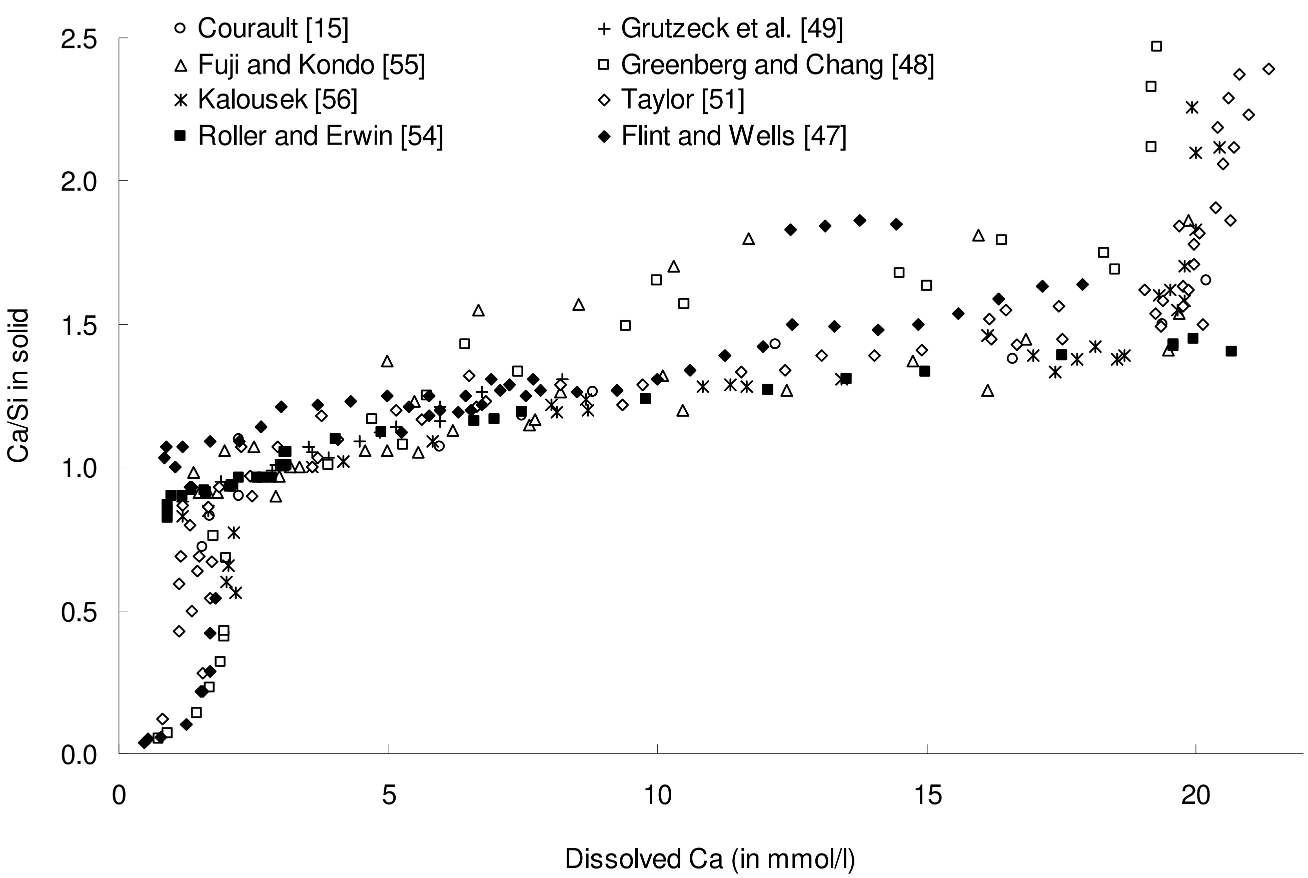
COMPOSITION OF AMORPHOUS CSH PHASES (2/4)



Dispersion in the values can be link to :

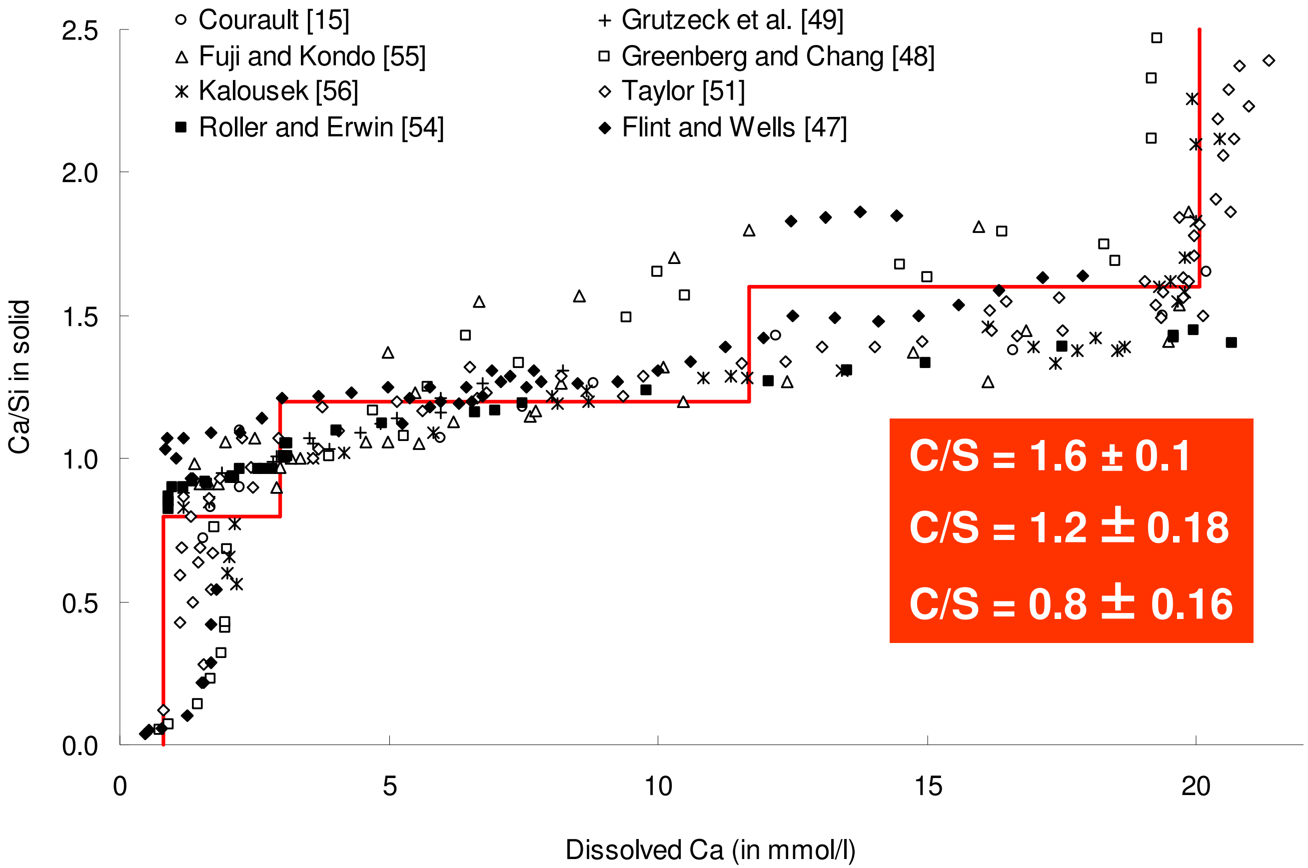
✓The synthesis route followed

✓The pathway followed to reach equilibrium (by dissolution or precipitation)

✓The assessment of the C/S ratio in the solid

✓A solid/liquid equilibrium not reached due to kinetic constraints

COMPOSITION OF AMORPHOUS CSH PHASES (3/4)



Blanc, P. et al. accepted. Chemical conceptual model for cement-based materials: Thermodynamic data assessment of stoichiometric and non-stoichiometric CSH phases. *J.Hazardous.Materials*

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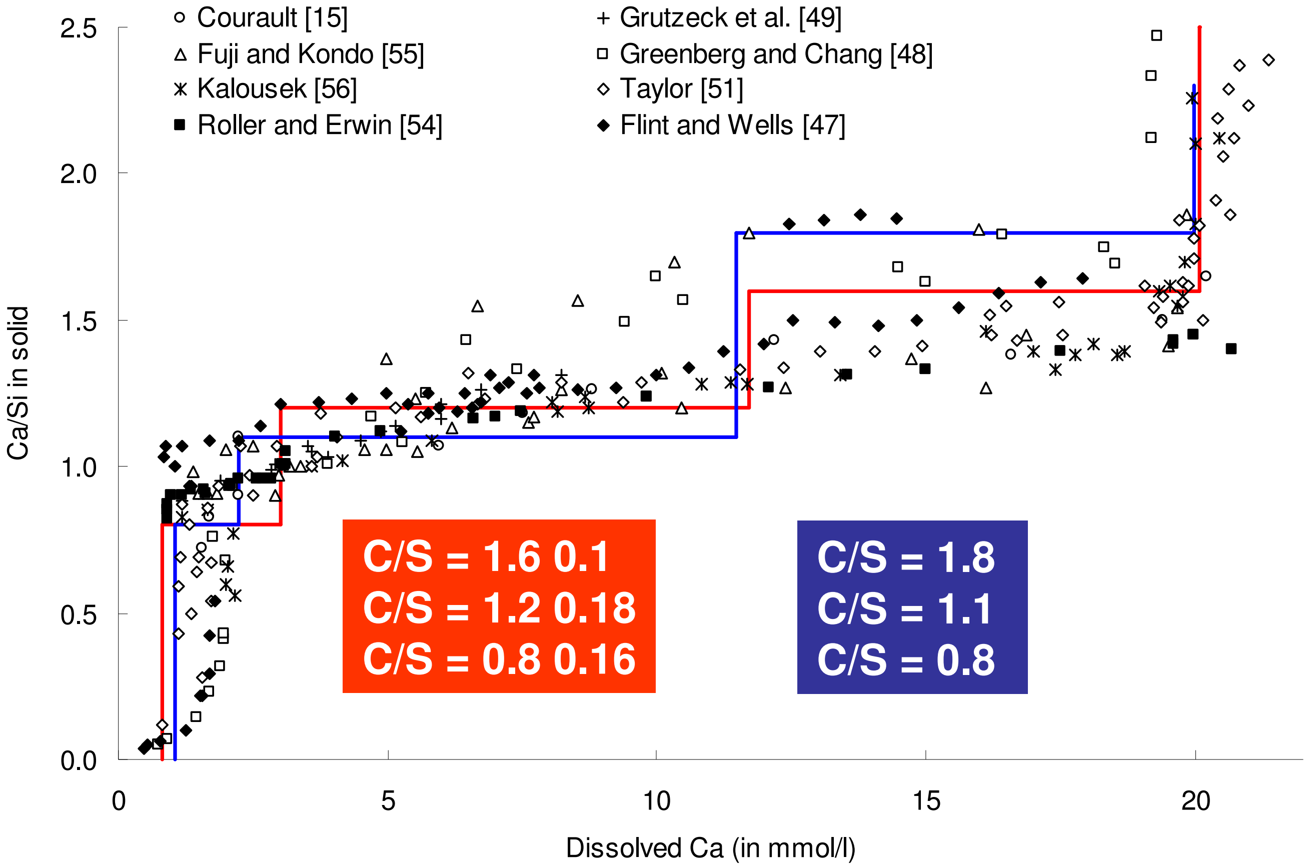
COMPOSITION OF AMORPHOUS CSH PHASES (3/4)



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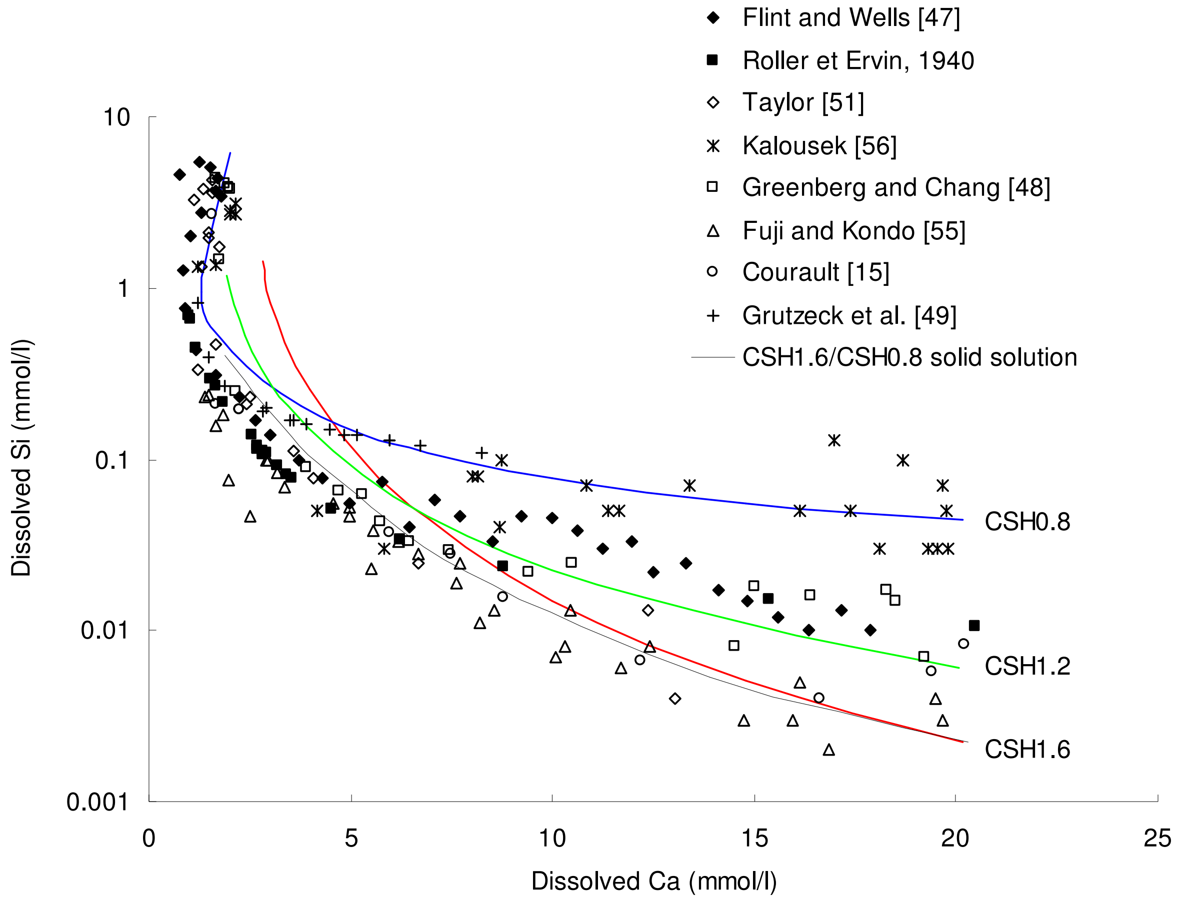
COMPOSITION OF AMORPHOUS CSH PHASES (4/4)



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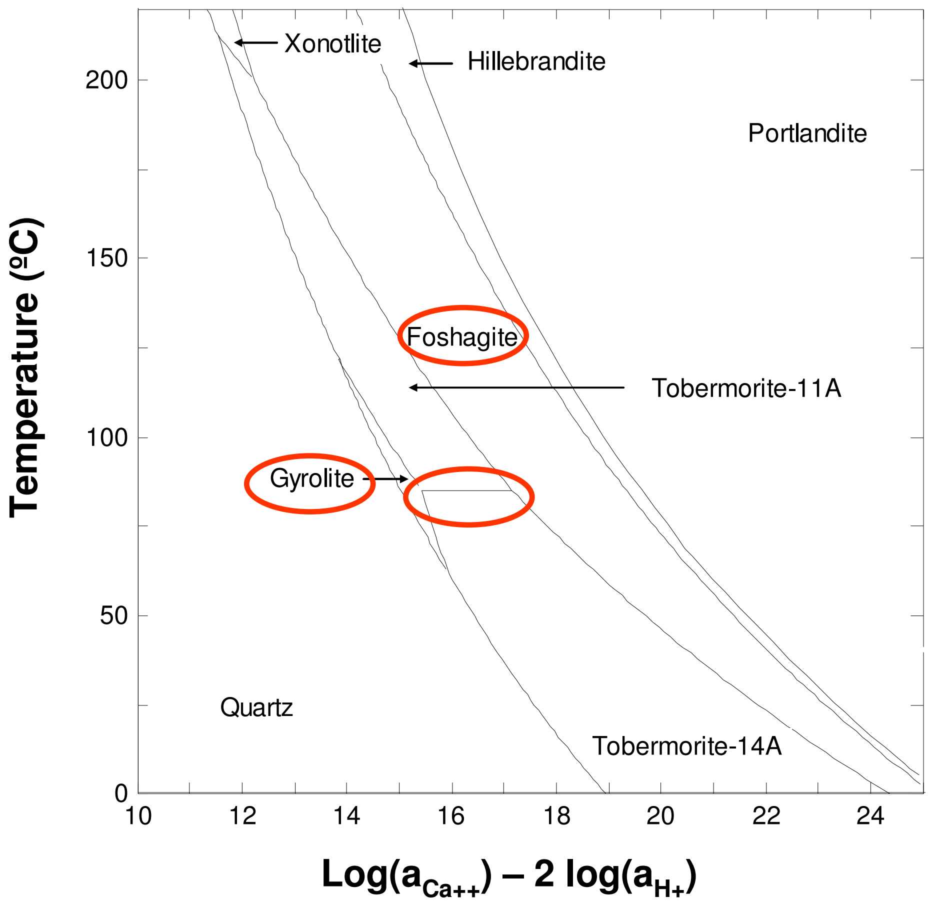
CRYSTALLINE CSH PHASES (1/2)



- ✓**Temperature transition to low**
- ✓**Authors see this phase at least up to 200℃**
- ✓**Foshagite considered as high temperature phase**
- ✓**Absence of okenite, afwillite and jennite**

Diagram calculated using the estimates of Babushkin et al. (EQ3.6)

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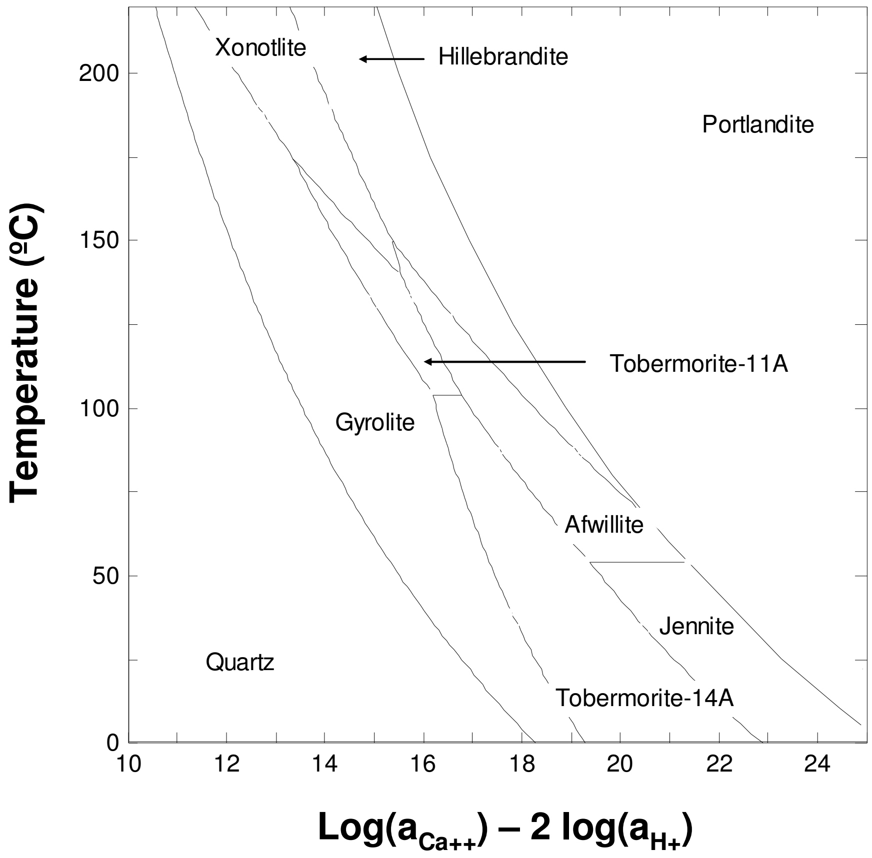
CRYSTALLINE CSH PHASES (2/2)



Hypotheses :

- ✓Use of triple point (Gibbs phases rule)
- ✓ΔH of Tobermorite 11A°, Xonotlite, Foshagite and Hillebrantite are fixed
- ✓The Cp of Babushkin were used

Phases	Température d'équilibre (°C)	Référence
AFW + POR + HIL	100 (100)	Hong et Glasser, 2004 Heller et Taylor, 1952
AFW + FOS + HIL	170 (169)	Hong et Glasser, 2004
AFW + XON + Hill	150 (150)	D'après Hong et Glasser, 2004 ; Atkinson et al., 1995
TOB11 + AFW + XON	140 (140)	El-Hemaly et al., 1977
TOB11 + TOB14	105 (104)	Maeshimae et al., 2003
TOB11 + XON + GYR	175 (174)	Kalousek et Nelson, 1978
JEN + Afwillite	T < 55°C (55)	Atkins et al., 1994
Tobermorite-14A, $LogK_{85°C}$ = 54.25 (54.25)		Atkinson et al., 1994
Jennite : 147.10 < $LogK_{25°C}$ < 150.81 (147.33)		Revertegat et al., 1997

Blanc, P. et al. accepted. *J.Hazardous.Materials*

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STARTING MINERALOGICAL CONDITIONS (CONCRETE)

Amorphous hypothesis @ 25ºC (1)

Mineral	Structural formula	Volume fraction	Concentration mol/L
C3FH6	$Ca_3Fe_2(OH)_{12}$	0.0216	0.94
Calcite	$CaCO_3$	0.7225	130.68
CSH1.6	$Ca_{1.6}SiO_{3.6}(H_2O)_{2.58}$	0.1373	10.83
Ettringite	$Ca_6Al_2(SO_4)_3(OH)_{12}(H_2O)_{26}$	0.0381	0.36
Hydrotalcite	$Mg_4Al_2O_7(H_2O)_{10}$	0.0041	0.12
KatoiteSi	$Ca_3Al_2(SiO_4)(OH)_8$	0.0135	0.64
Portlandite	$Ca(OH)_2$	0.0629	12.72

Cristalline hypothesis @ 25ºC (2)

Mineral	Structural formula	Volume fraction	Concentration mol/L
C3AH6	$Ca_3Al_2(OH)_{12}$	0.0144	0.66
C3FH6	$Ca_3Fe_2(OH)_{12}$	0.0216	0.96
Calcite	$CaCO_3$	0.7154	130.15
Ettringite	$Ca_6Al_2(SO_4)_3(OH)_{12}(H_2O)_{26}$	0.0396	0.37
Hydrotalcite	$Mg_4Al_2O_7(H_2O)_{10}$	0.0042	0.12
Jennite	$Ca9Si6H_{22}O_{32}$	0.1329	1.97
Portlandite	$Ca(OH)_2$	0.0729	13.24

	Hyp1	**Hyp2**
Element	Concentration mmol/L	
Al	$2.3\ 10^{-2}$	$4.93\ 10^{-2}$
C	$7.46\ 10^{-3}$	$4.46\ 10^{-3}$
Ca	$2.02\ 10^{1}$	$2.02\ 10^{1}$
Cl	$4.10\ 10^{1}$	$4.10\ 10^{1}$
Fe	$6.05\ 10^{-5}$	$1.25\ 10^{-4}$
K	$8.35\ 10^{-1}$	$8.35\ 10^{-1}$
Mg	$4.56\ 10^{-6}$	$3.11\ 10^{-6}$
Na	$4.58\ 10^{1}$	$4.58\ 10^{1}$
S	$2.08\ 10^{-2}$	$1.85\ 10^{-2}$
Si	$2.49\ 10^{-3}$	$1.70\ 10^{-4}$
Sr	$2.01\ 10^{-1}$	$2.01\ 10^{-1}$
pH	12.5	

Pore water composition after resaturation with COX pore water

CEM I + calcite aggregate

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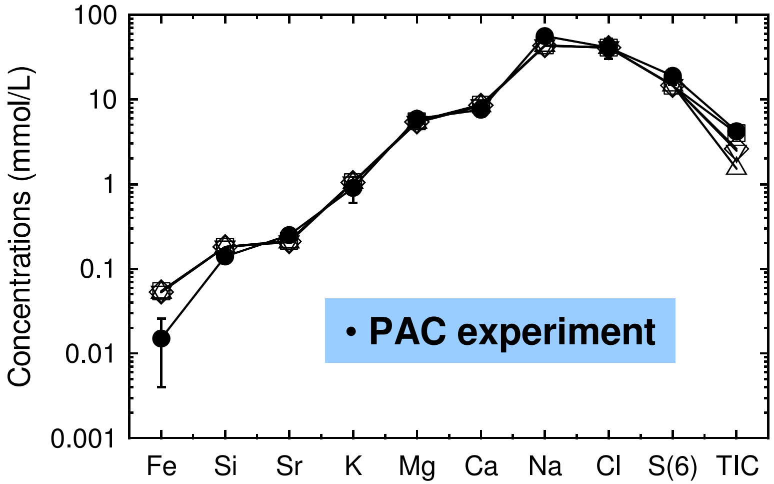
STARTING MINERALOGICAL CONDITIONS (COX)

Mineral	Structural formula	Volume fraction	mol/L
Calcite	$CaCO_3$	0.2262	27.89
Celestite	$SrSO_4$	0.0067	0.66
Chlorite	$Fe_5Al(AlSi_3)O_{10}(OH)_8$	0.0167	0.36
Dolomite	$CaMg(CO_3)_2$	0.0408	2.90
Illite	$K_{0.85}Mg_{0.25}Al_{2.35}Si_{3.4}O_{10}(OH)_2$	0.3406	10.74
Feldspath K	$K(AlSi_3)O_8$	0.0312	1.31
Smectite	$Ca_{0.01}Na_{0.434}K_{0.026})(Si_{3.612}Al_{0.388})Al_{1.608}Fe_{0.222}Mg_{0.228})O_{10}(OH)_2;5.441H_2O$	0.0765	2.62
Pyrite	FeS_2	0.0053	1.01
Quartz	SiO_2	0.2465	49.50
Siderite	$FeCO_3$	0.0095	1.47
Porosity	0.18		

Element	Concentration (mmol/KgW)
Al	$6.93\ 10^{-6}$
Fe	$4.84\ 10^{-2}$
Si	0.18
Sr	0.21
K	0.83
Mg	5.58
Ca	8.80
Na	45.80
Cl	41.00
S(6)	16.30
TIC	2.53
pH	7.21



• **PAC experiment**

Gaucher et al. Submitted to GCA

STARTING MINERALOGICAL CONDITIONS (MX80 bentonite)

Mineral	Structural formula	Volume Fraction	mol/L
Plagioclase	$NaAlSi_3O_8$	0.0683	1.27
Calcite	$CaCO_3$	0.0061	0.31
Dolomite	$CaMg(CO_3)_2$	0.0000	0.00
Feldspath K	$K(AlSi_3)O_8$	0.0151	0.26
Smectite	$Ca_{0.01}Na_{0.434}K_{0.026})(Si_{3.612}Al_{0.388})Al_{1.608}Fe_{0.222}Mg_{0.228})O_{10}(OH)_2;5.441H_2O$	0.5454	7.55
Pyrite	FeS_2	0.0197	0.17
Quartz	SiO_2	0.3327	27.23
Siderite	$FeCO_3$	0.0028	0.18
Porosity	**0.35**		

Element	Concentration (mmol/KgW)
Al	$4.43\ 10^{-5}$
Ca	$6.25\ 10^{-2}$
Cl	$4.01\ 10^{1}$
Fe	$8.43\ 10^{-3}$
K	$3.46\ 10^{-1}$
Mg	$3.78\ 10^{-2}$
Na	$1.01\ 10^{2}$
S	$1.64\ 10^{1}$
Si	$1.92\ 10^{-1}$
Sr	$9.72\ 10^{-4}$
TIC	$2.66\ 10^{1}$
pH	8.40

70% MX80 + 30% Sand

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- **….**

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TRANSPORT PARAMETERS

Material	**Effective** diffusion coefficient ($m^2.s^{-1}$)	Porosity	**Poral** diffusion coefficient ($m^2.s^{-1}$)
Concrete (amorphe)	$9.0\ 10^{-12}$	0.135	$6.67\ 10^{-11}$
Concrete (cristalline)	$9.0\ 10^{-12}$	0.135	$6.67\ 10^{-11}$
Bentonite (MX80)	$1.0\ 10^{-11}$	0.37	$2.70\ 10^{-11}$
COX	$1.0\ 10^{-11}$	0.18	$5.56\ 10^{-11}$

$$D_{0,T} = D_{0,298} \cdot \frac{T}{298} \cdot \frac{\eta_{298}}{\eta_T}$$

$$\eta_T = \exp^{\ln 10 * (-1.37023.(tc-20) + \frac{8.36.10^{-4}.(tc-20)^2}{109+tc})}$$

Ratio 2.54 between 70°C and 25°C

1D cartesian saturated conditions: PHREEQC

1D radial non-saturated conditions: TOUGHREACT

✓**The release of the MCD option in PHREEQC permits to treat multi-porosity cases**

✓**However, MCD option still under improvement : => use of Mix Cells instead**

cf. Appelo et al. (2008) Journal of Contaminant Hydrology Vol 101 pp 67

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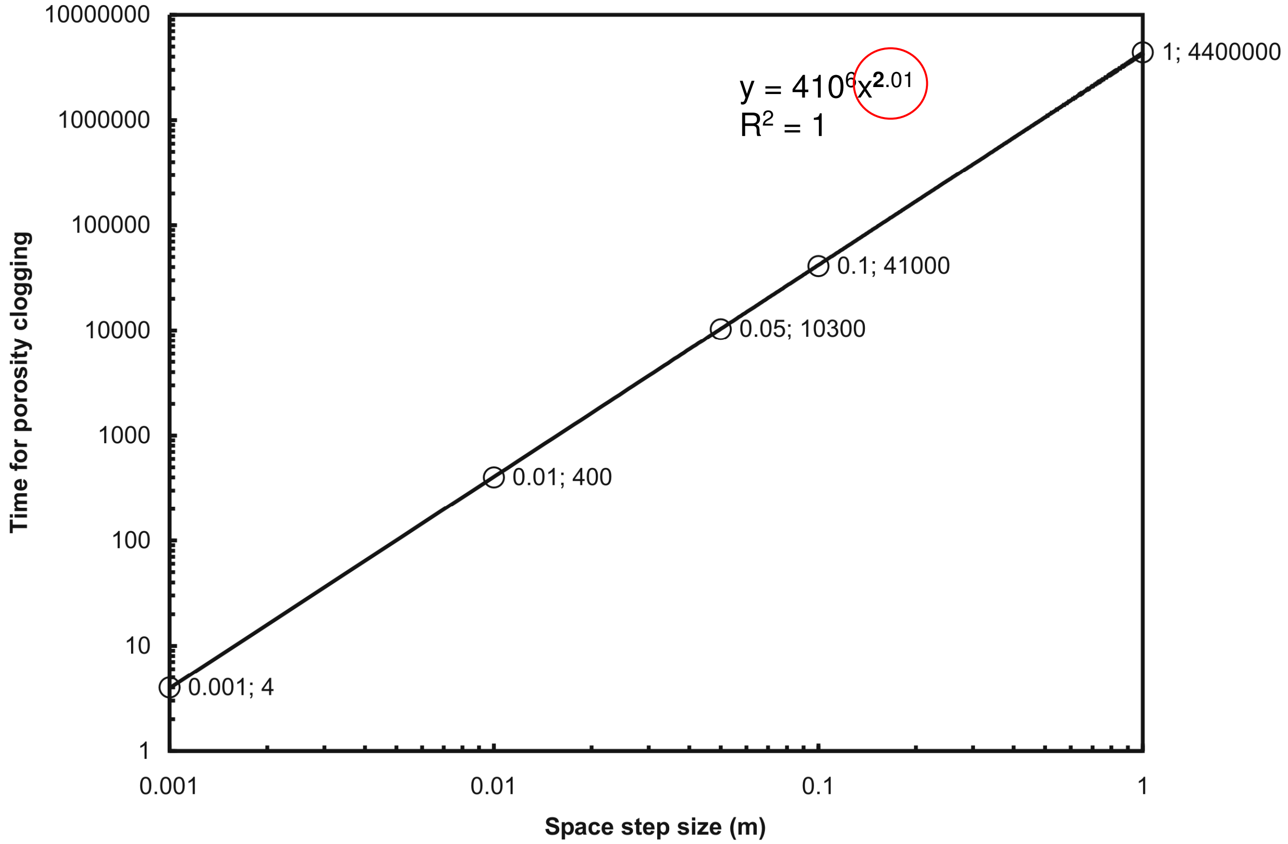
INFLUENCE OF MESH SIZE (at local equilibrium)



Diffusion controlled :

$$x^2 = Dt$$

$$2\log x = \log D + \log t$$

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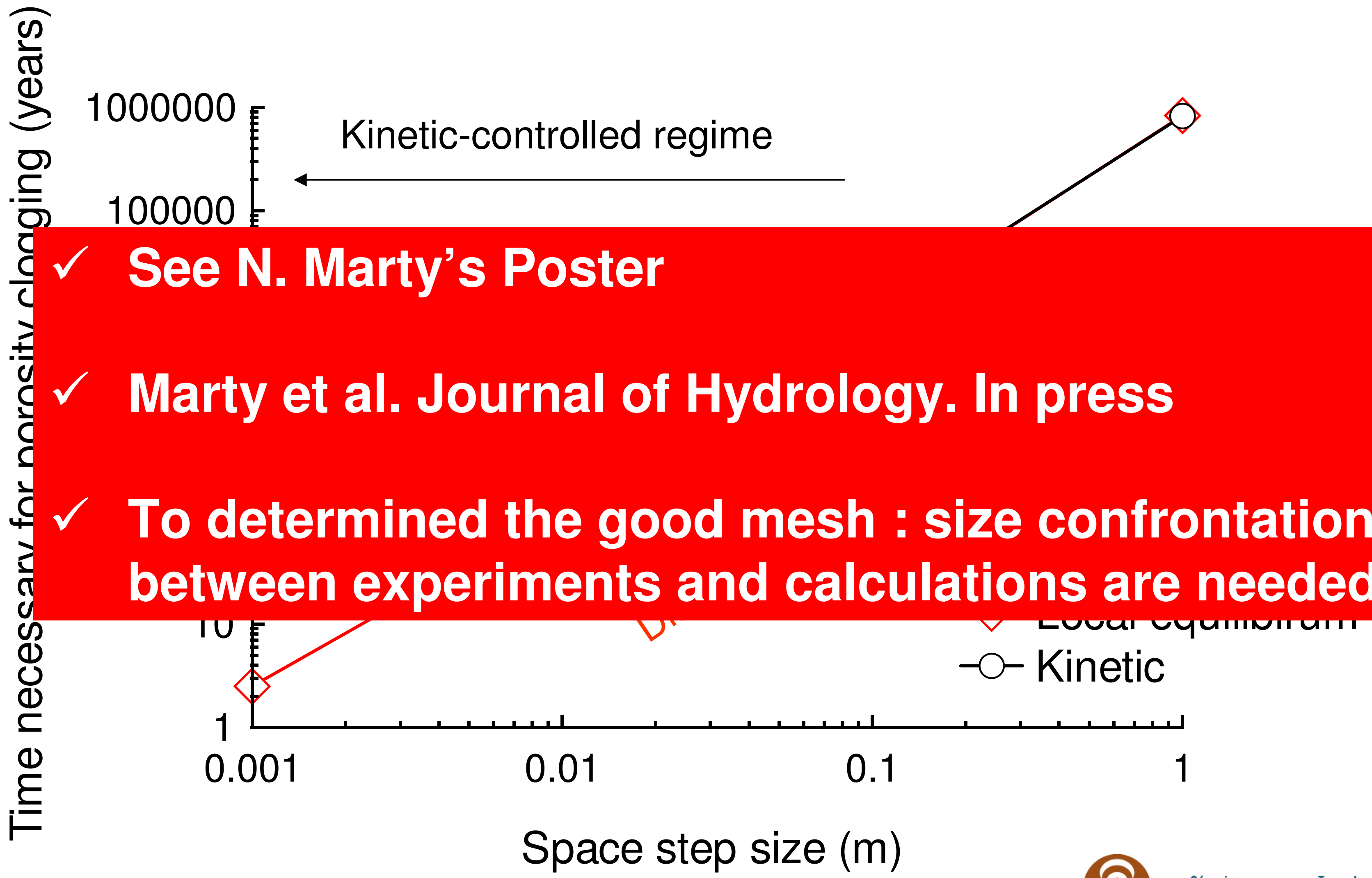
INFLUENCE OF MESH SIZE



- ✓ **See N. Marty's Poster**
- ✓ **Marty et al. Journal of Hydrology. In press**
- ✓ **To determined the good mesh : size confrontation between experiments and calculations are needed**

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> **….**

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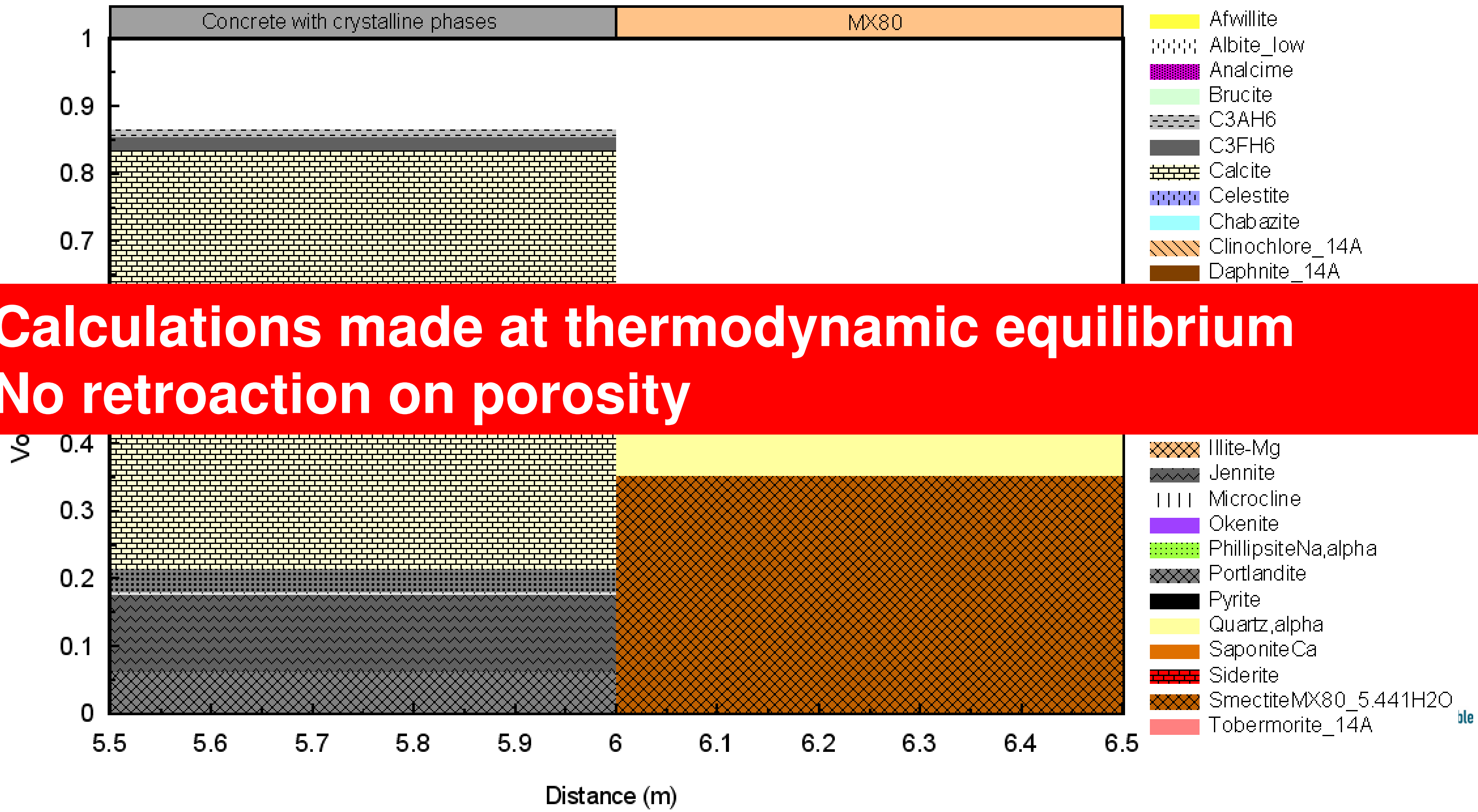
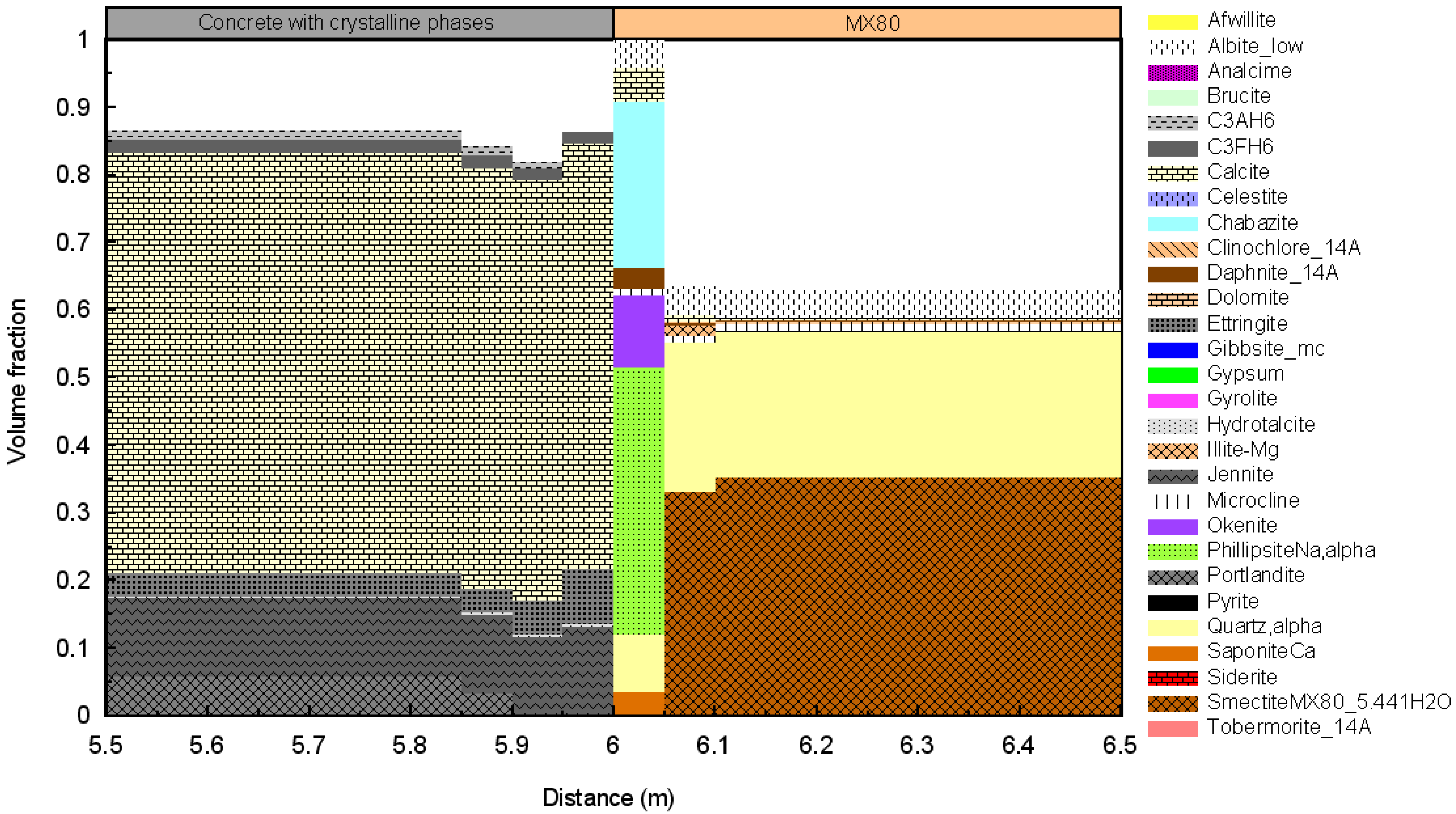
Concrete with crystalline CSH	MX80
6 m	6 m
De 9.10^{-12} m^{2}s^{-1}	De 1.10^{-11} m^{2}s^{-1}
pH 12.5 @ 25 ºC	pH 8.2 @ 25 ºC

t=0



1. **Calculations made at thermodynamic equilibrium**
2. **No retroaction on porosity**

Time for porosity clogging = 2700 years



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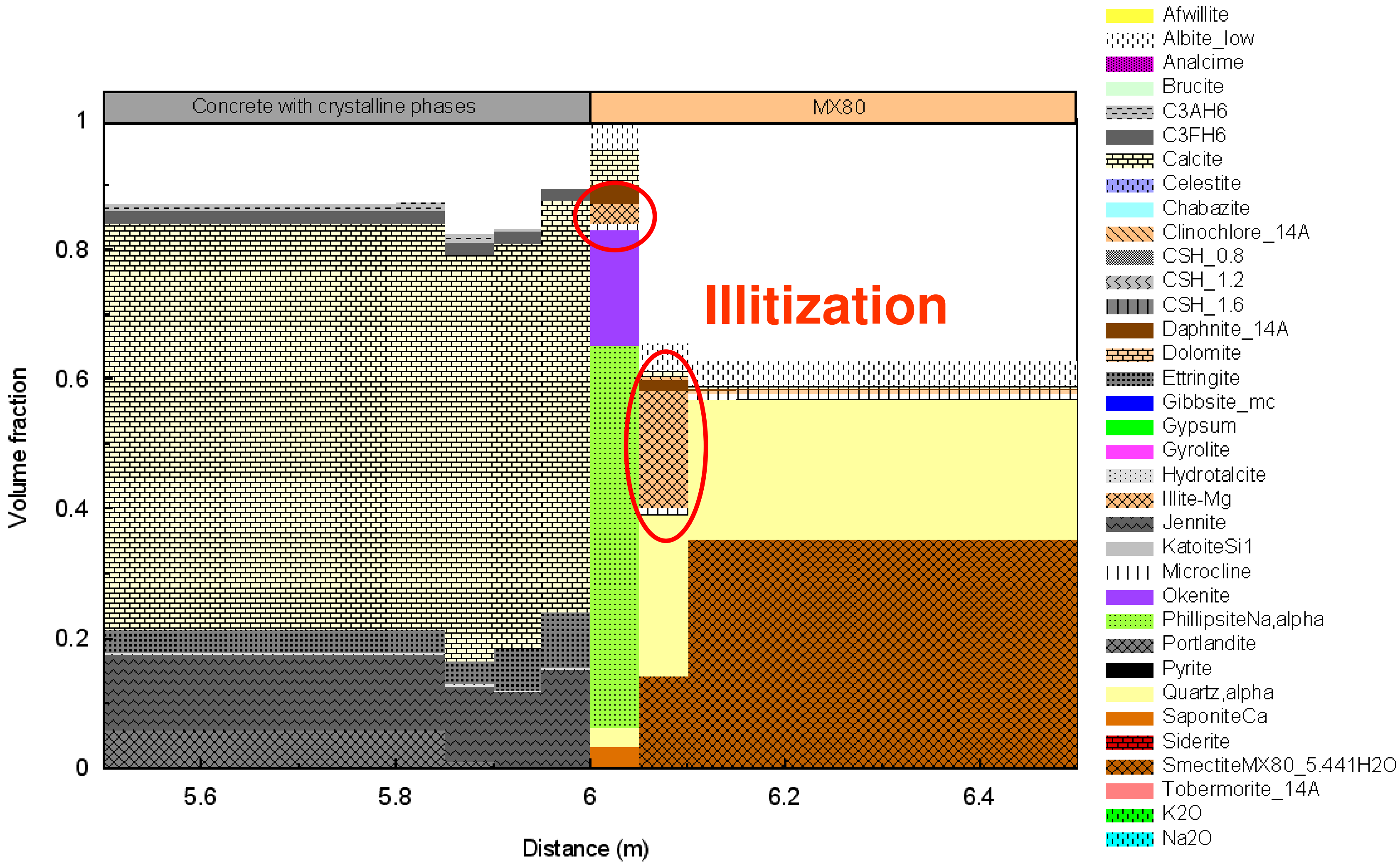
« Young » concrete pH13.2 Time for porosity clogging 3500 ans



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TEMPERATURE INFLUENCE ON CLOGGING

Clay Zeolite CSH

25 ºC

MX80		Concrete with amorphous CSH	Concrete with crystalline CSH
Clogging	Time	10 300 ± 100 years	2700 ± 100 years
	Cell	Concrete	MX80
Extension		30 cm	15 cm
		20 cm	10 cm
Dissolution		Portlandite, Hydrotalcite Katoite C	Portlandite, C3AH6
		Smectite, quartz	Smectite, quartz, dolomite
Precipitation		CSH1.2, CSH0.8, Ettringite, Clinc	Ettringite, jennite
		Analcime, calcite, chabazite, daphnite, (illite), phi Na, saponiteCa	Calcite, cl e, daphnite, (illite), okenite, phillipsite

Clogging time ratio 2.6

Clogging time ratio 1.7

70 ºC

MX80		Concrete with amorphous CSH	Concrete with crystalline CSH
Clogging	Time	3960 ± 10 years	1600 ± 100 years
	Cell	MX80	MX80
Extension		30 cm	15 cm
		25 cm	15 cm
Dissolution		Portlandite, C3FH6, ettringite, CSH1.6, katoite	Portlandite, ettrinngite, C3AH6, hydrotal
		Smectite, quartz, dolomite	Smectite, quartz, dolomite
Precipitation		CSH1.2, CSH0.8, daphnite, ettringite	afwillite, Clinochlore, ettringite
		Calcite, chabazite, daphnite, (illite), phillipsiteNa, saponiteCa	Calcite, chabazite, daphnite, gyrolite, (illite), phillipsite

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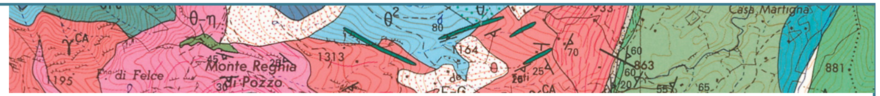
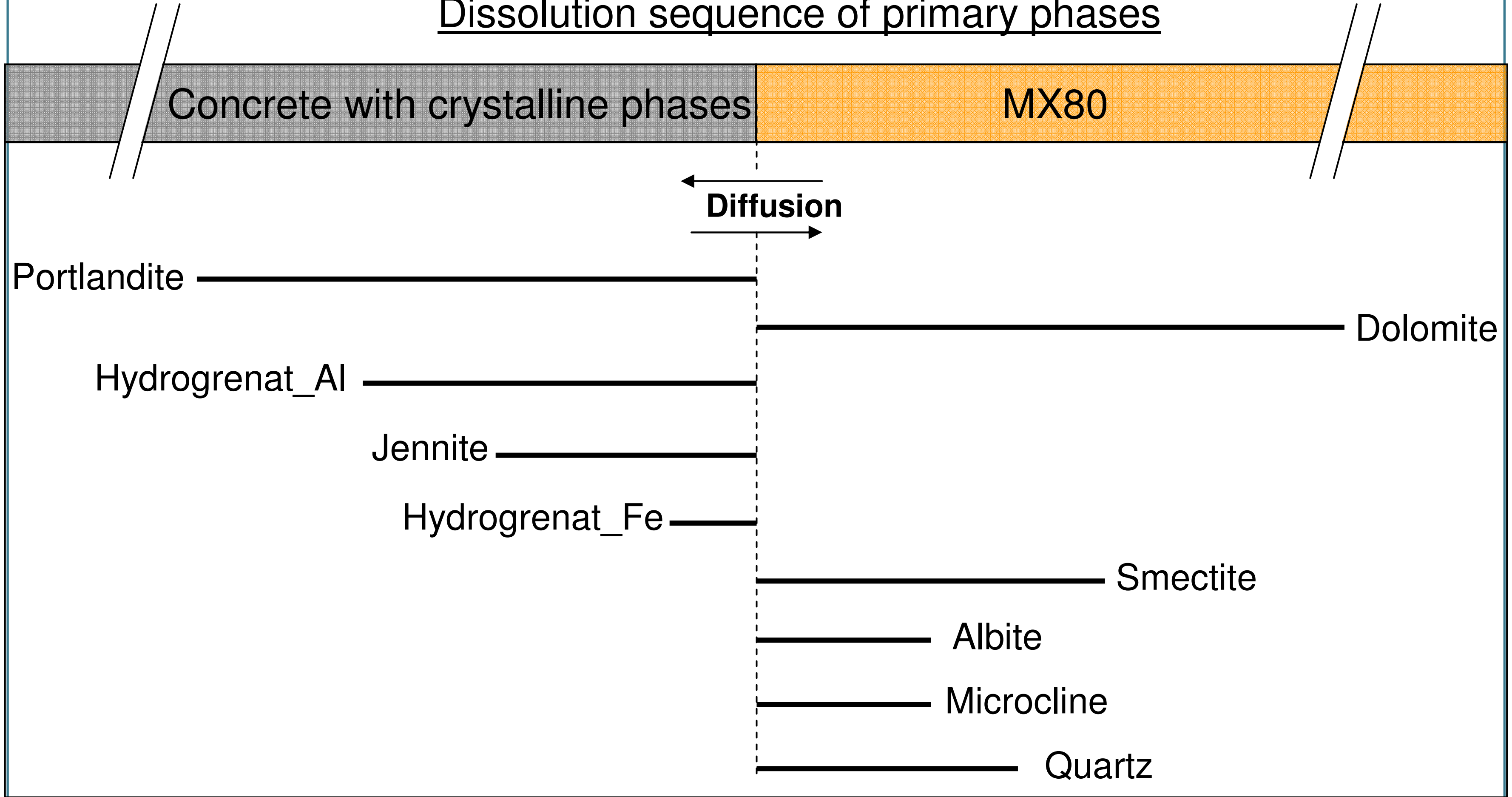
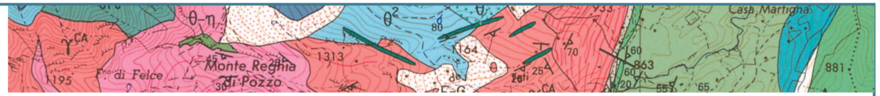


Dissolution sequence of primary phases

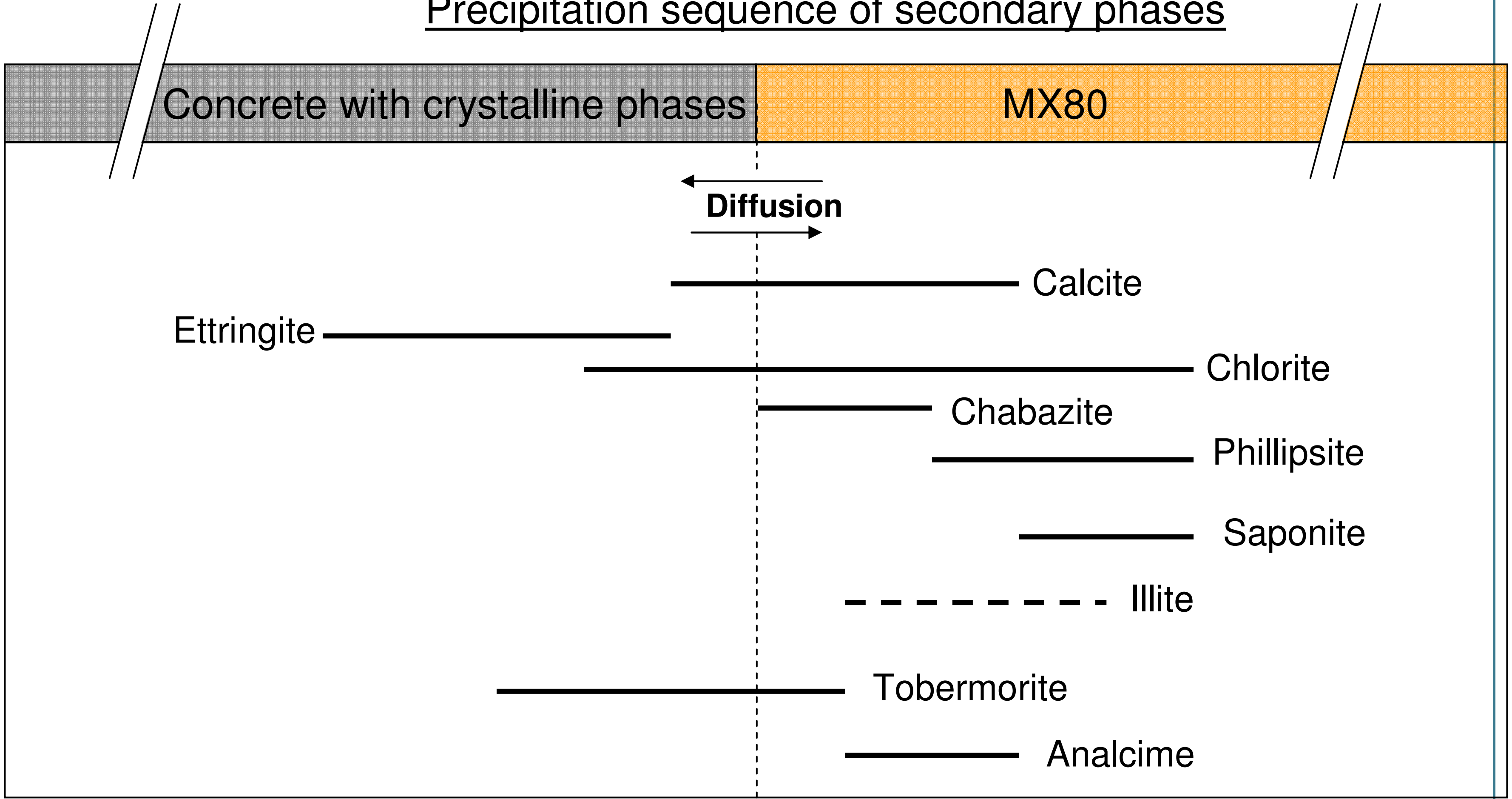


Altered zone: less than 50 cm

at the clogging time



Precipitation sequence of secondary phases



Altered zone: less than 50 cm

at the clogging time

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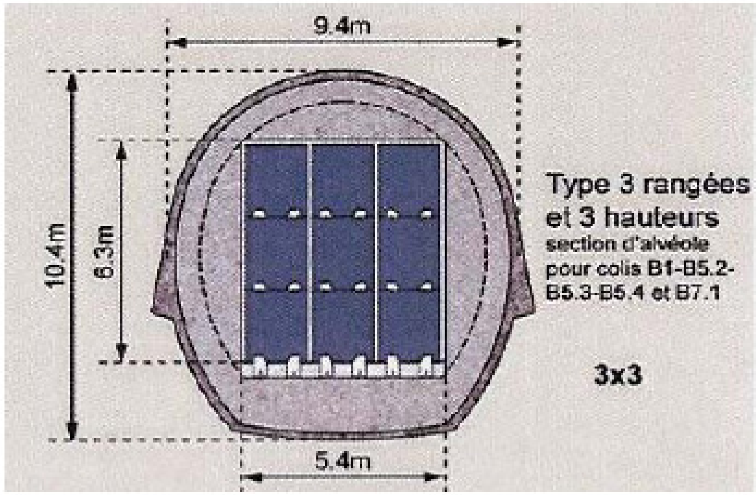
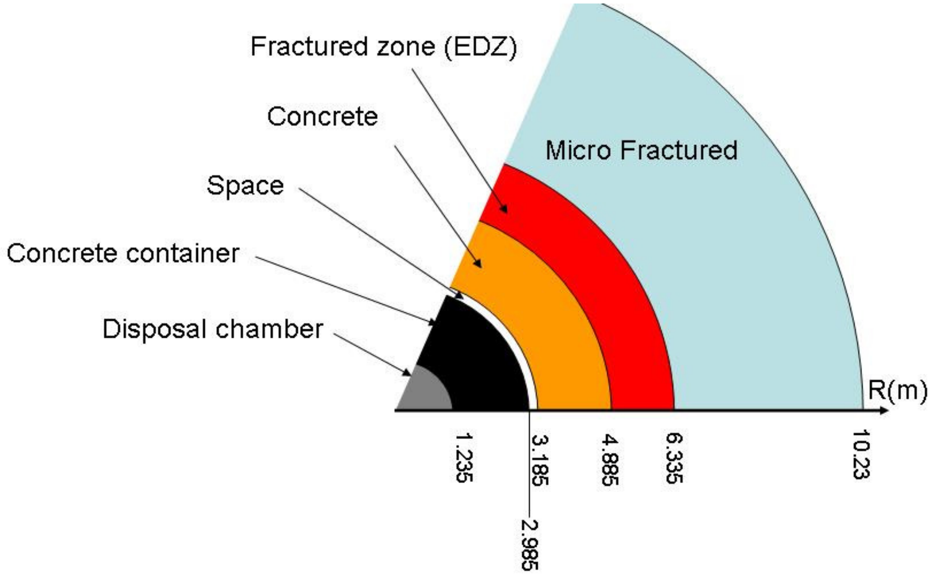
TOWARD A MORE REALISTIC GEOMETRY





Name	Calculated radius (m)	Chosen radius in the mesh (m)	Difference (%)	Number of mesh
R_{Cp}	1,234	1,235	0,08%	1 of 1.235 m
R_{BC}	2,985	2,985	0,00%	35 of 5 cm
R_{jext}				4 of 5cm
R_{BR}				34 of 5 cm
R_{ZF}				29 of 5 cm
R_{MF}				87 of 5cm
$R_{Cox\ Sai...}$				60 mesh of variable length

Space :

- **Saturated case : concrete porewater**
- **Non Saturated case : air**

✓Hypothesis of volume conservation

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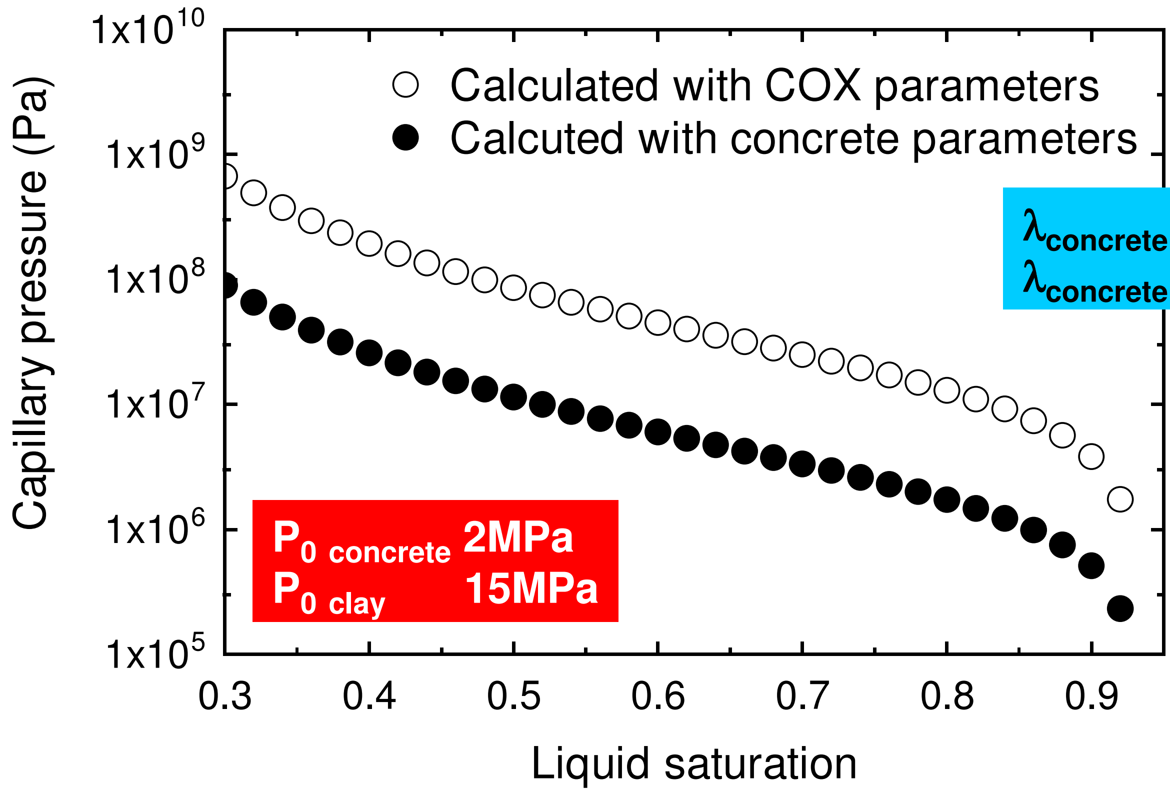
CAPILLARY PRESSURE FONCTION

NON SATURATED CONDITIONS

$$P_{cap} = -P_0([S^*]^{\frac{-1}{\lambda}} - 1)^{1-\lambda} \quad S^* = \frac{S_l - S_{lr}}{S_{ls} - S_{lr}}$$

Van Genuchten function



$\lambda_{concrete}$ and λ_{clay} slightly different
$\lambda_{concrete}$ ~0.35 and λ_{clay} ~0.33

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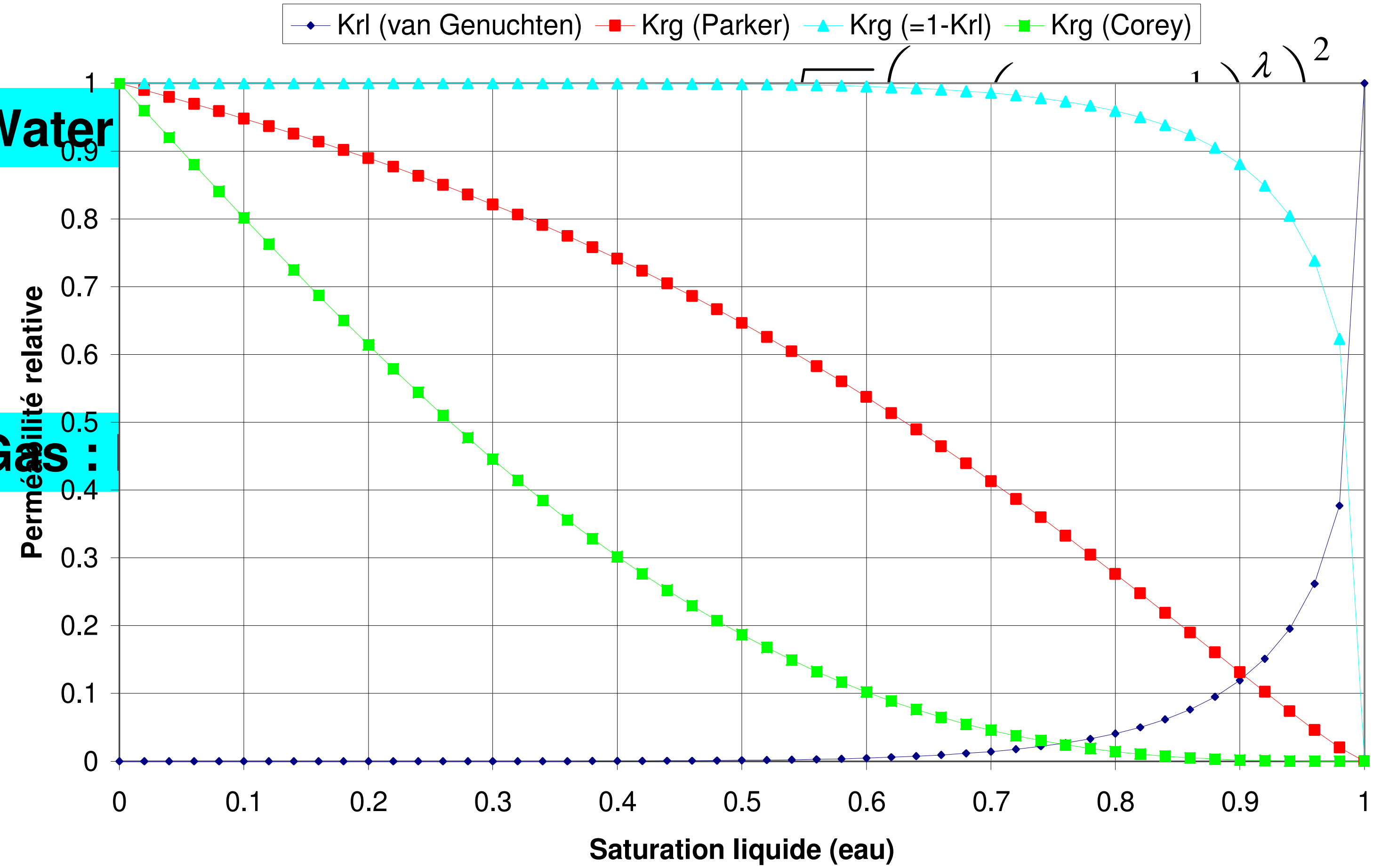
RELATIVE PERMEABILITY FUNCTION

✓ Water

✓ Gas :



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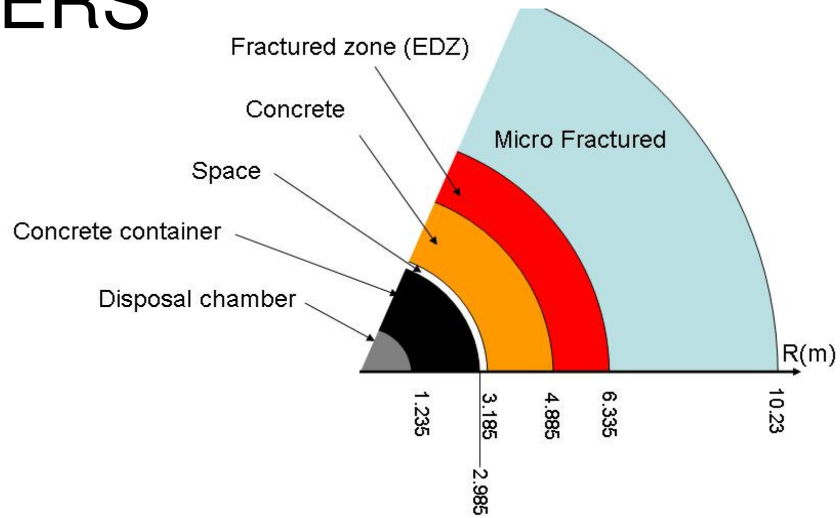
TRANSPORT PARAMETERS



Material	Permeability K (ms^{-1})	Porosity (%)	Effectif diffusion coefficient (m^2s^{-1})	
COX	$1,6\ 10^{-13}$	18	10^{-11}	(ANDRA, 2005d)
Microfractured	$5,0\ 10^{-11}$	18	10^{-11}	(ANDRA, 2005d)
EDZ	$5,0\ 10^{-9}$	20	2.10^{-11}	(ANDRA, 2005d)
Concrete containers	10^{-11}	13,5	2.10^{-12}	Munier (2008)
Concrete	10^{-10}	13,0	9.10^{-12}	Munier (2008)
Space	$1,0\ 10^{-8}$	100	2.10^{-09}	

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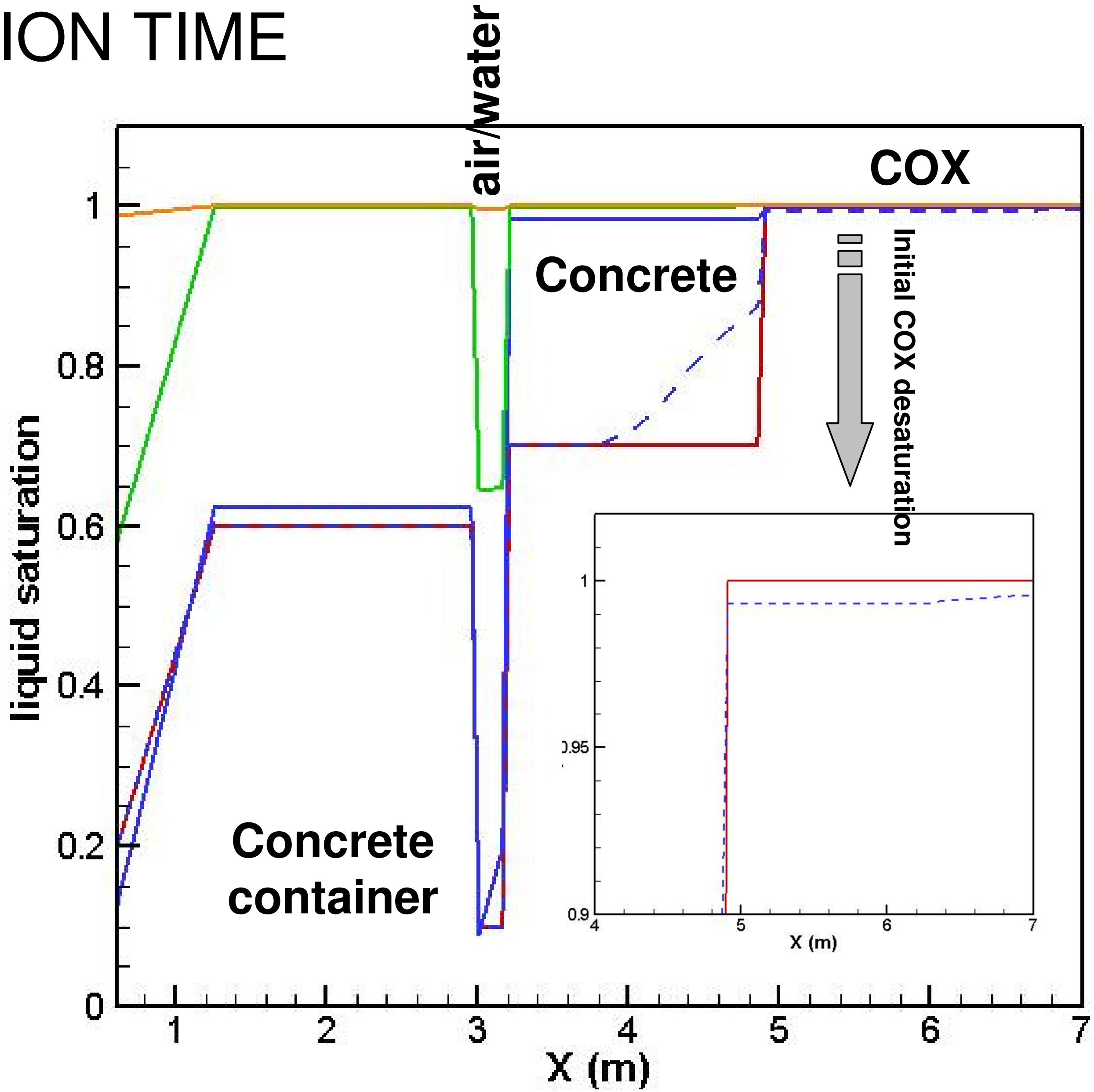
RESATURATION TIME

- Initial
- 0.1 y
- 100 y
- 500 y
- 1000 y



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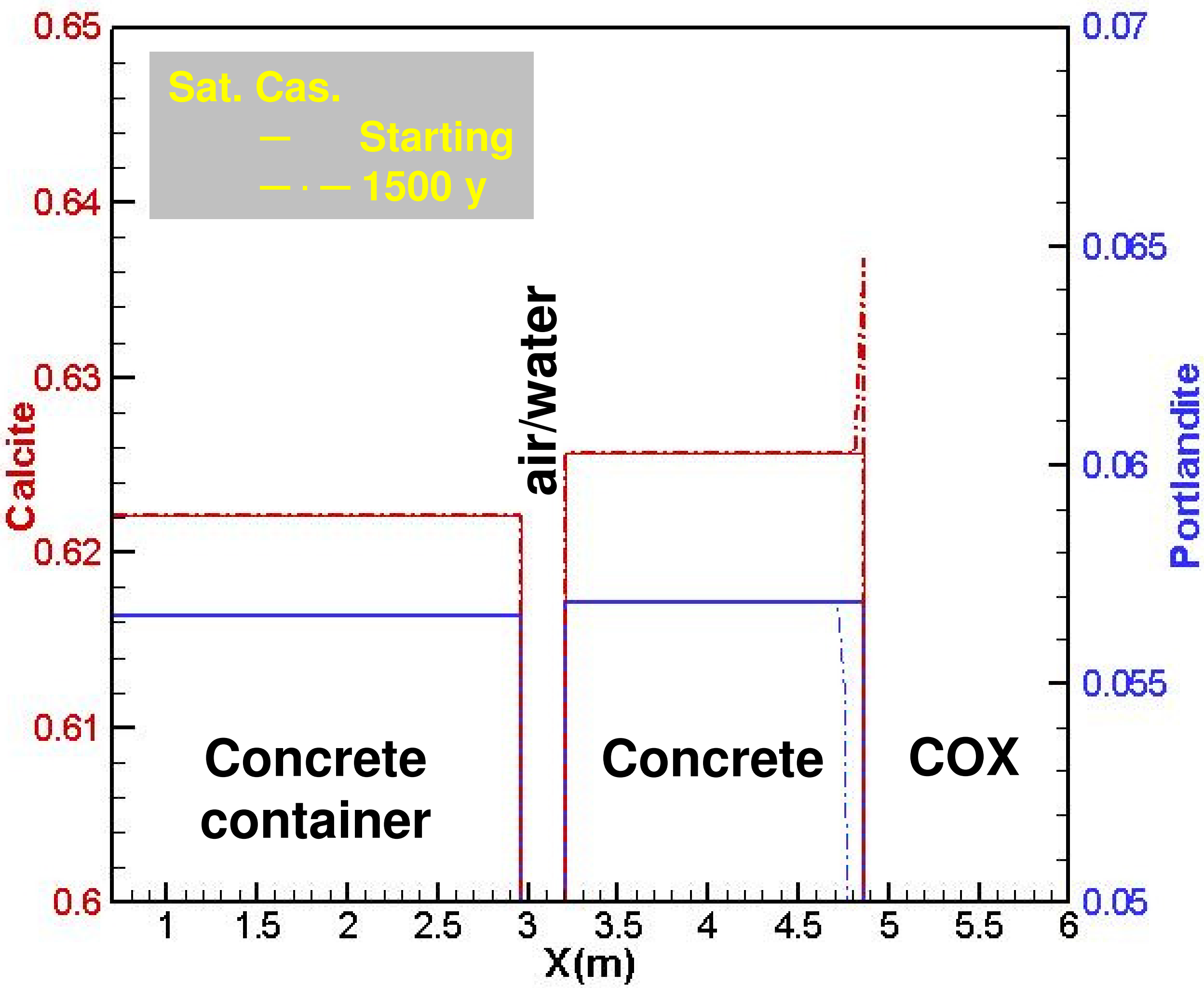
SATURATED CONDITIONS



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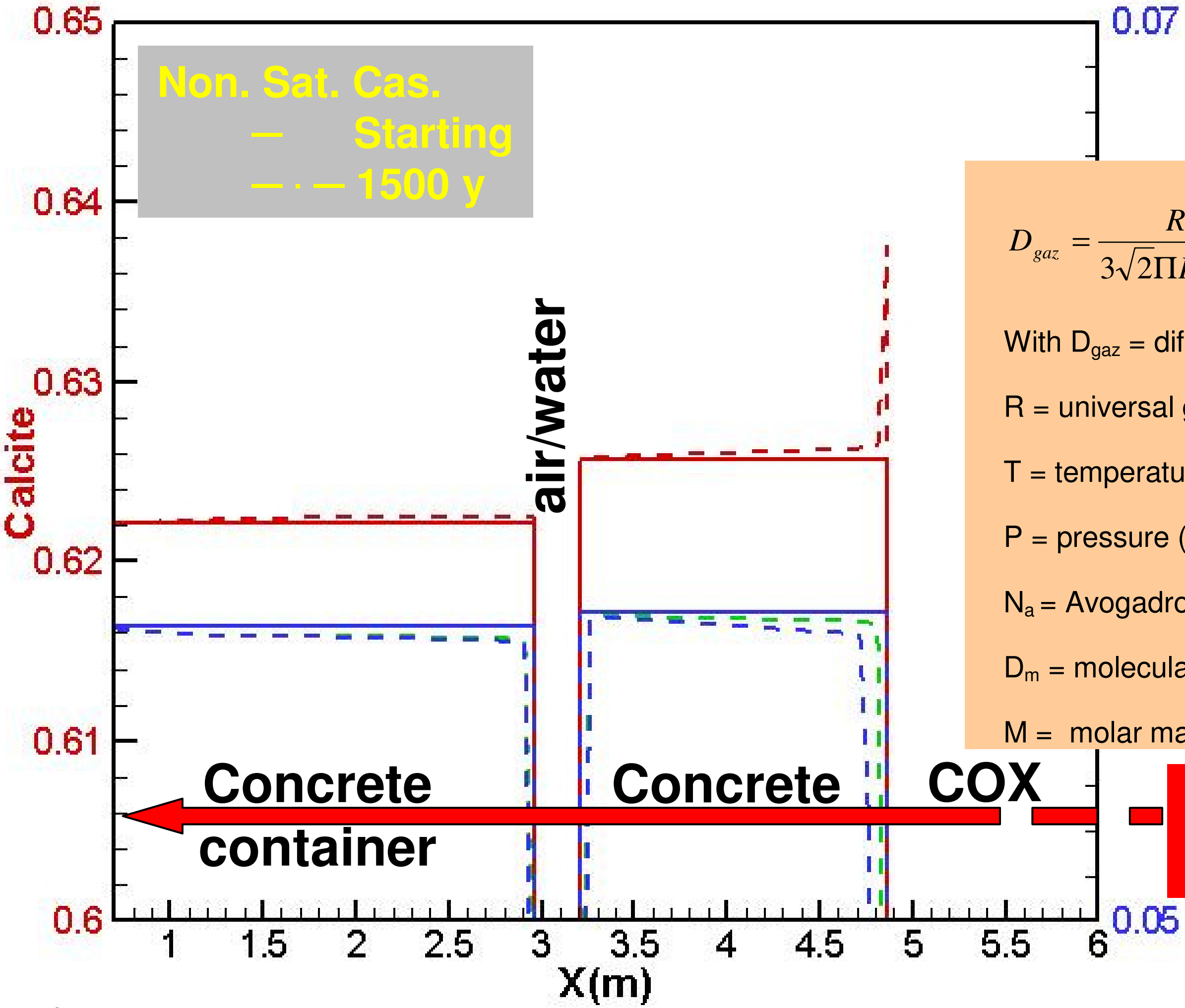
NON SATURATED CONDITIONS



$$D_{gaz} = \frac{RT}{3\sqrt{2}\Pi P N_a d_m^2}\sqrt{\frac{8RT}{\Pi M}}$$

With D_{gaz} = diffusion coefficient (m^2/s)

R = universal gaz constant (8,31451 $m^2 kgs^{-2} mol^{-1} K^{-1}$)

T = temperature in Kelvin

P = pressure ($kgm^{-1}s^{-2}$)

N_a = Avogadro number (6,0221367.10^{23} molecules/mol)

D_m = molecular diameter (m)

M = molar mass (kg/mol)

Carbonation due to CO_2 gas diffusion

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CRITICAL ELEMENTS FOR THE MODELLING

- **A coherent thermodynamic database to work in temperature**
- **A "complete" mineralogical description of the initial system**
- **Transport parameters (porosities, permeabilities, diffusion coefficients, heat conductivities…)**

- **Transport reactive calculation**
  - PHREEQC (1D)
  - TOUGHREACT (radial geometry, non saturated condition, thermal gradient….)
- **Experiments to test and improve the modelling**
- **….**

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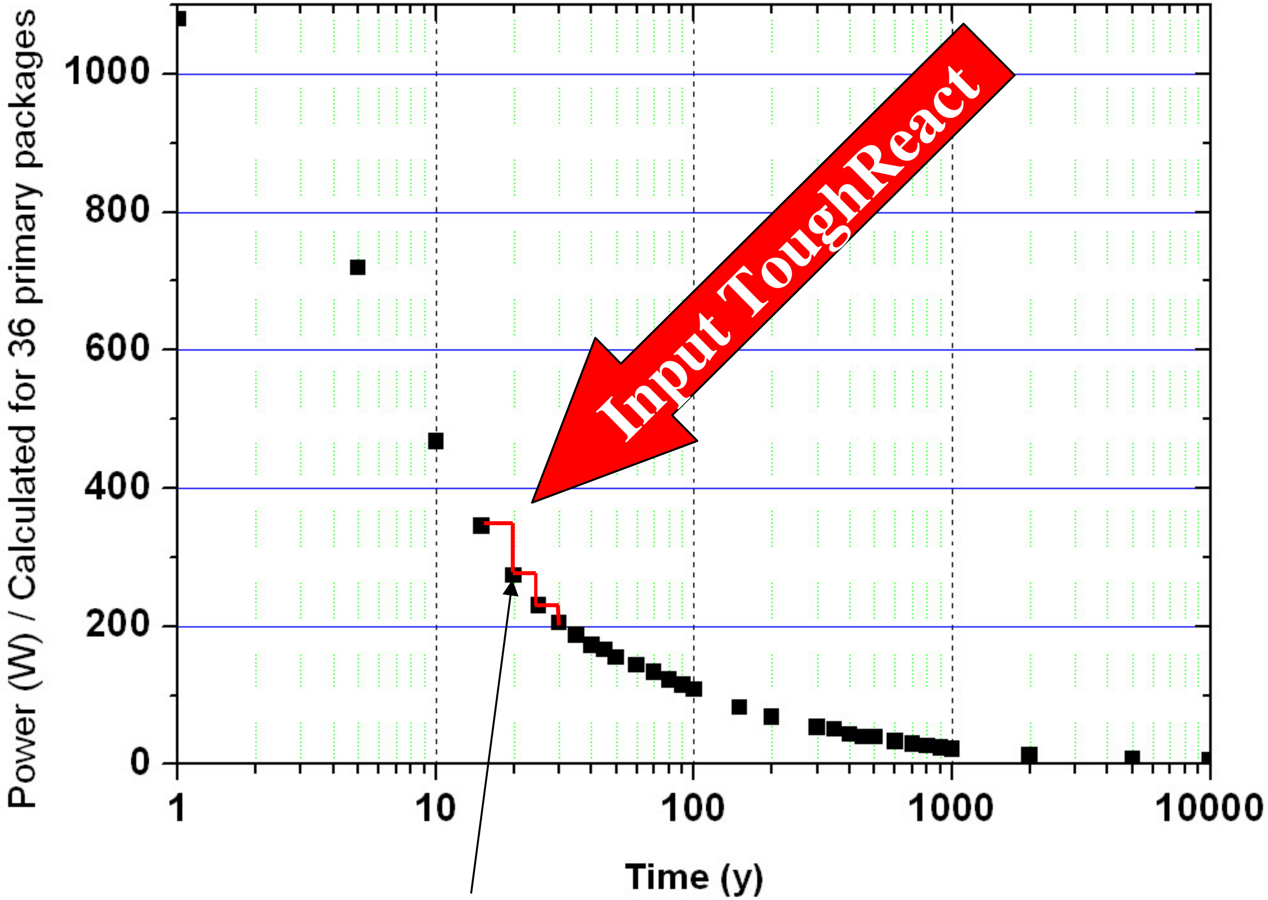
TRANSIENT THERMAL STATE



270 W after 20 years

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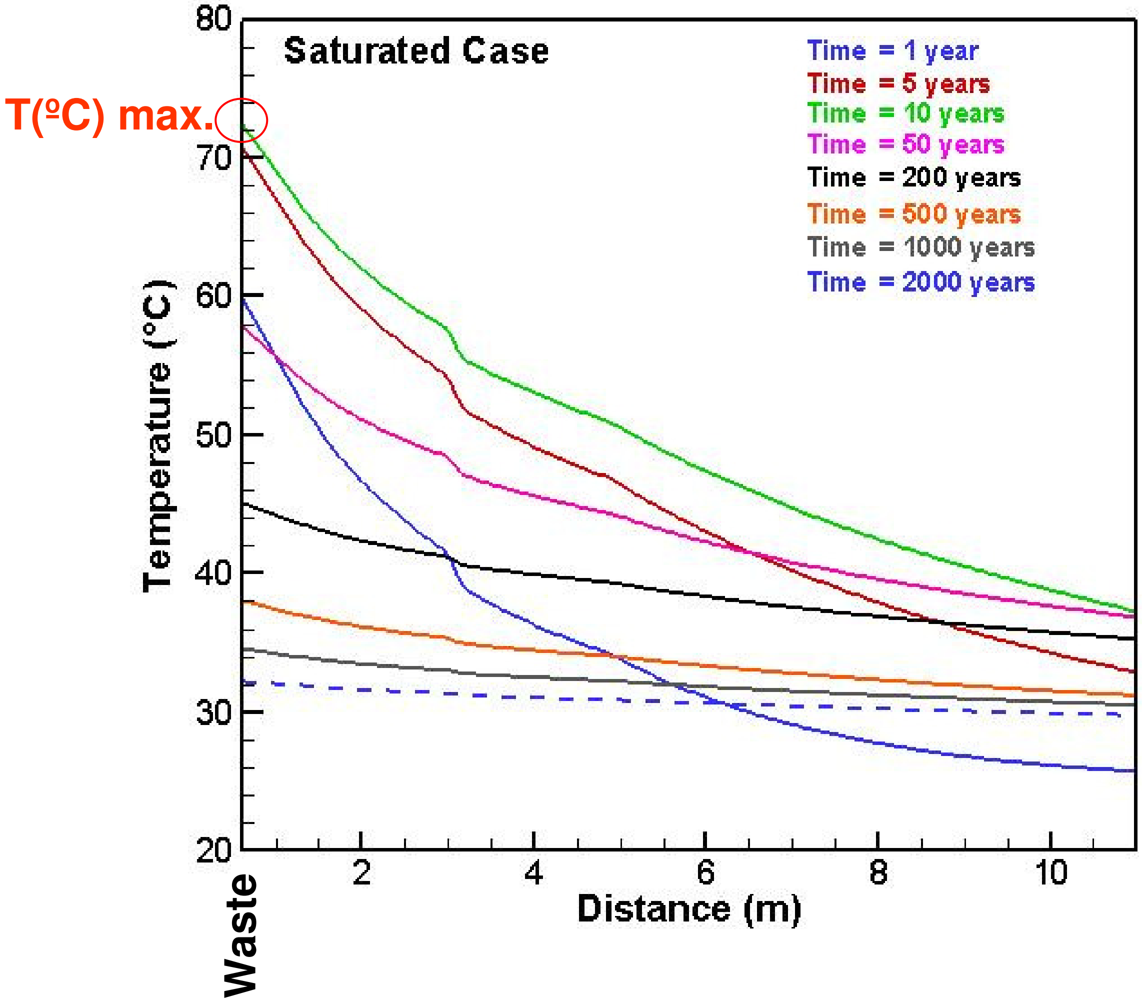
TEMPERATURE EVOLUTION



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CONCLUSIONS

- **Alteration of concrete/clay: limited in space (~50cm) with saturated conditions and clogging**

- **Clogging porosity is mesh size dependent at local equilibrium**

- **Transient states (non-saturated period, thermal period) : ~ 2000 years**

- **Carbonation: increased by CO_2(g) diffusion in non-saturated conditions**

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OUTLOOK

> **Fully coupled reactive transport considering complex mineralogy and complex geometry with both non-saturated and non-isothermal conditions**

> **Simulation of fractures of EDZ (due to excavation) by "Multiple INteracting Continua" (MINC function of TOUGH2)**

> **Kinetics instead of local equilibrium**

> **Archie law: retroaction of chemical reactions on effective diffusion coefficient**

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