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# Modelling approach to the evolution of physicochemical conditions in deep geological repository: alteration of engineered materials and redox control

Olivier Bildstein, P. Thouvenot, J. E. Lartigue, B. Cochepin, I. Munier

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DE LA RECHERCHE À L'INDUSTRIE



**MODELLING APPROACH TO THE  
EVOLUTION OF PHYSICOCHEMICAL  
CONDITIONS IN DEEP GEOLOGICAL  
REPOSITORY:  
ALTERATION OF ENGINEERED MATERIALS  
AND CLAYSTONES - REDOX CONTROL**

O. Bildstein, P. Thouvenot, J.E. Lartigue

CEA (French Alternative Energies and Atomic Energy Commission)

B. Cochepin, I. Munier

Andra (French Radioactive Waste Management Agency)

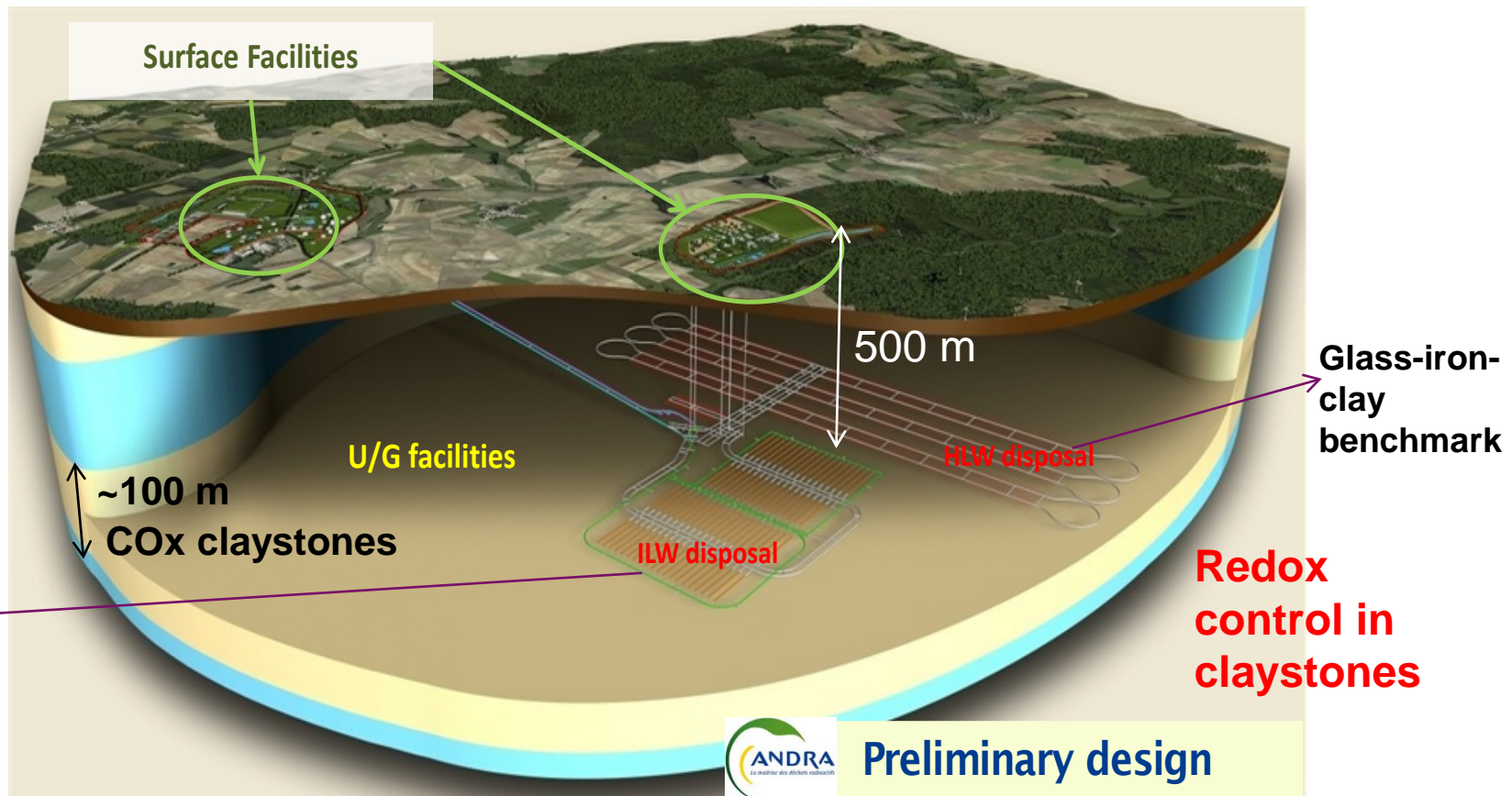


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SeS BENCH V – A CORUÑA - OCTOBER 13-15, 2016

# DISPOSAL CONCEPT IN A CLAYSTONE FORMATION

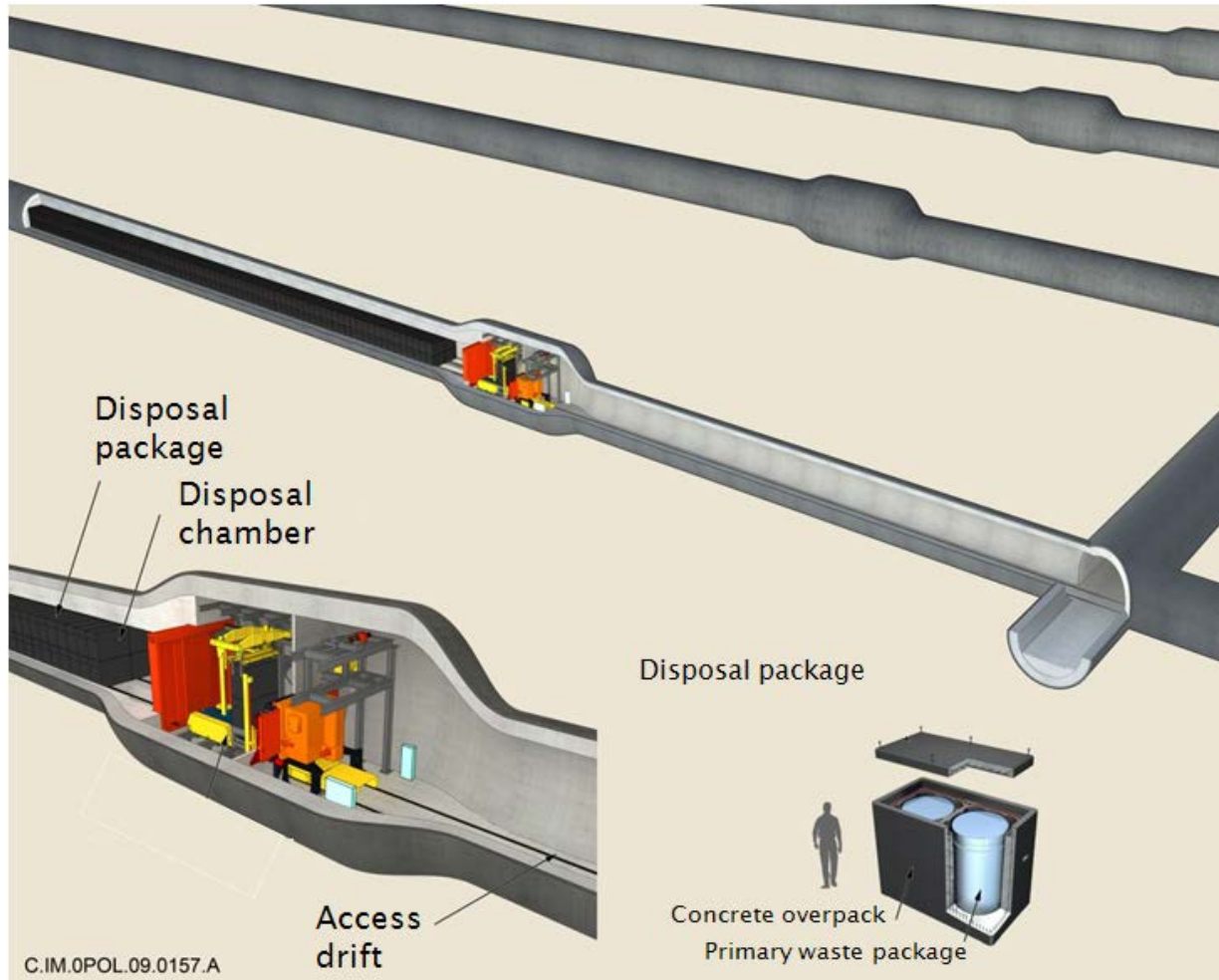
Current design of deep underground repository for high and intermediate level long-lived waste



**Update of the  
atmospheric concrete  
carbonation benchmark**

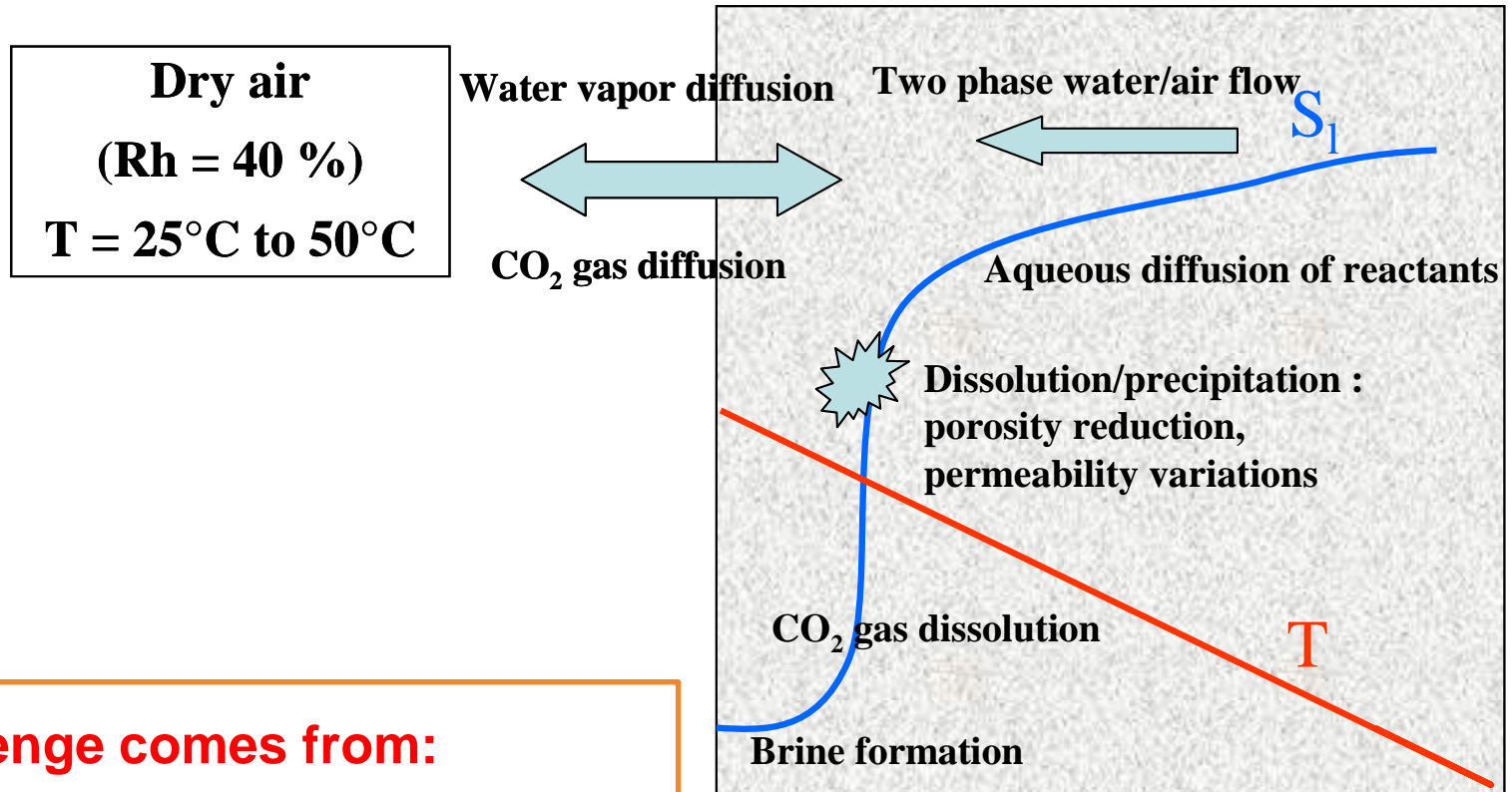
# DESIGN: ILLW CELLS, SHAFTS (AND SEALS), ILLW DISPOSAL OVERPACK

Atmospheric carbonation of overpack during the operating period



- **Bitumized waste**
- **Compacted metallic waste**
- **Organic waste**

# DRYING AND CARBONATION PROCESSES OF ILLW OVERPACK

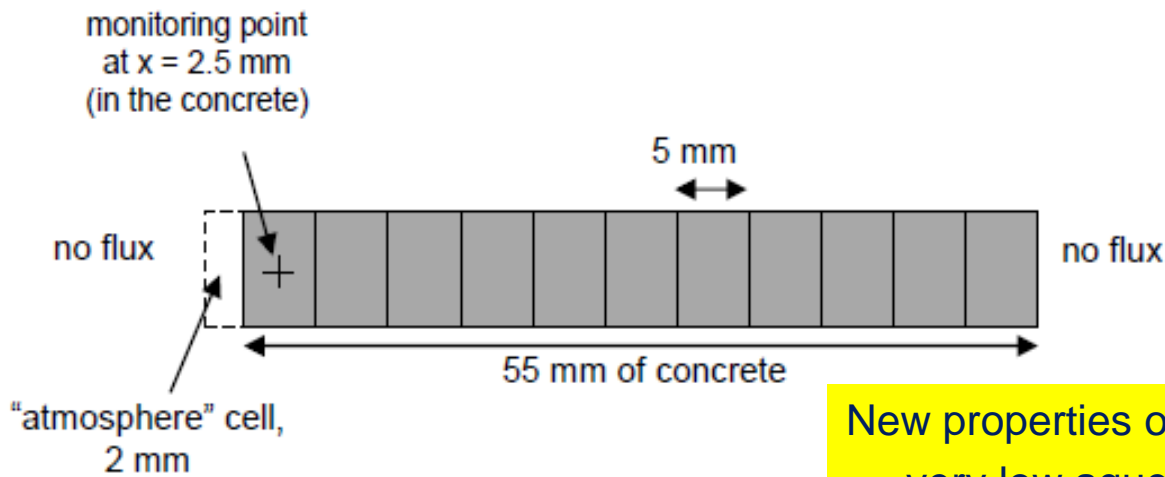


## Major challenge comes from:

- CO<sub>2</sub> fast gaseous transport and high reactivity with portlandite and CSH
- Coupling capability with « multiphase » flow and transport

# GEOMETRY + BOUNDARY CONDITIONS

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



New properties of « atmosphere cell » :

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

Full multiphase codes :

Toughreact (CEA + T. Xu, JLU)

iCORE (J. Samper, UDC)

HYTEC ??

Drying with Richards' equation :

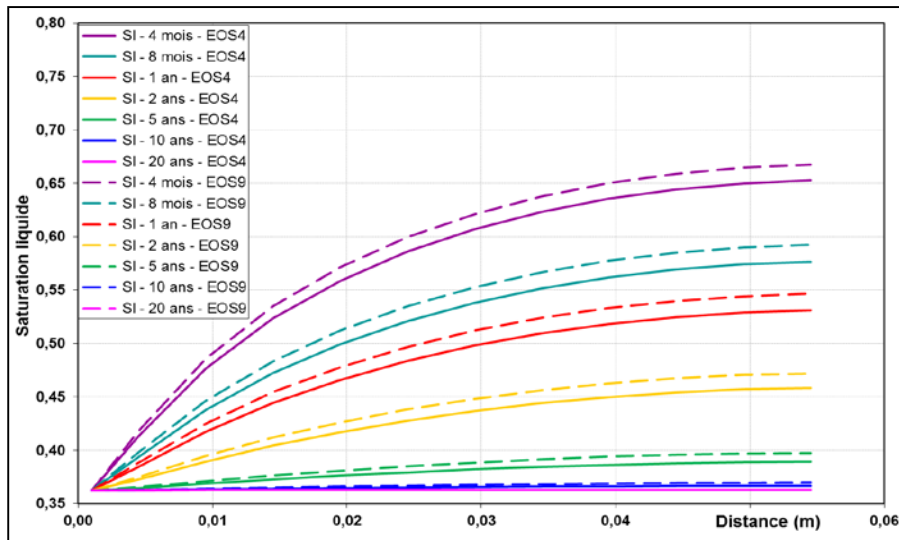
MIN3P (S. Béa, CONICET ; U. Mayer, UBC)

HYTEC (J. Corvisier, Mines Paristech)

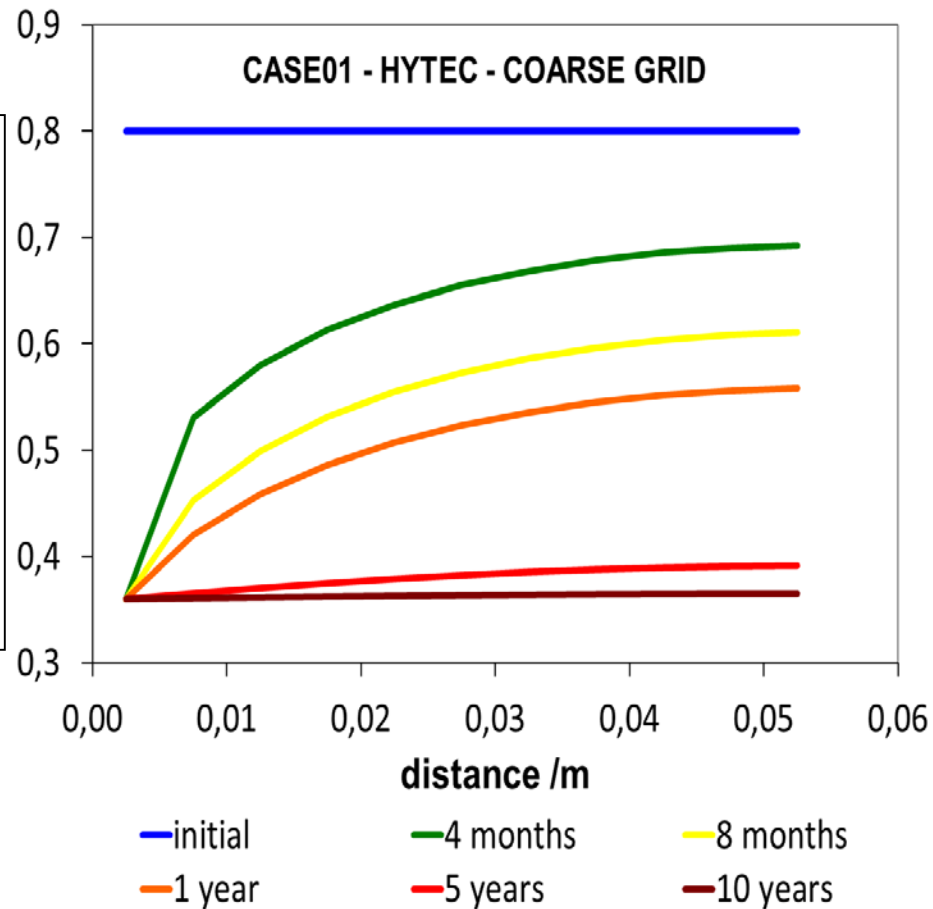
Crunchflow (CEA + C. Steefel, LBNL)



# COMPONENT 1: DRYING RESULTS



**TOUGH2**  
**Full multiphase (EOS4)**  
**Richards (EOS9)**



**Hytec (Richards' equation)**

→ OK to use Richards' equation for benchmarking exercise



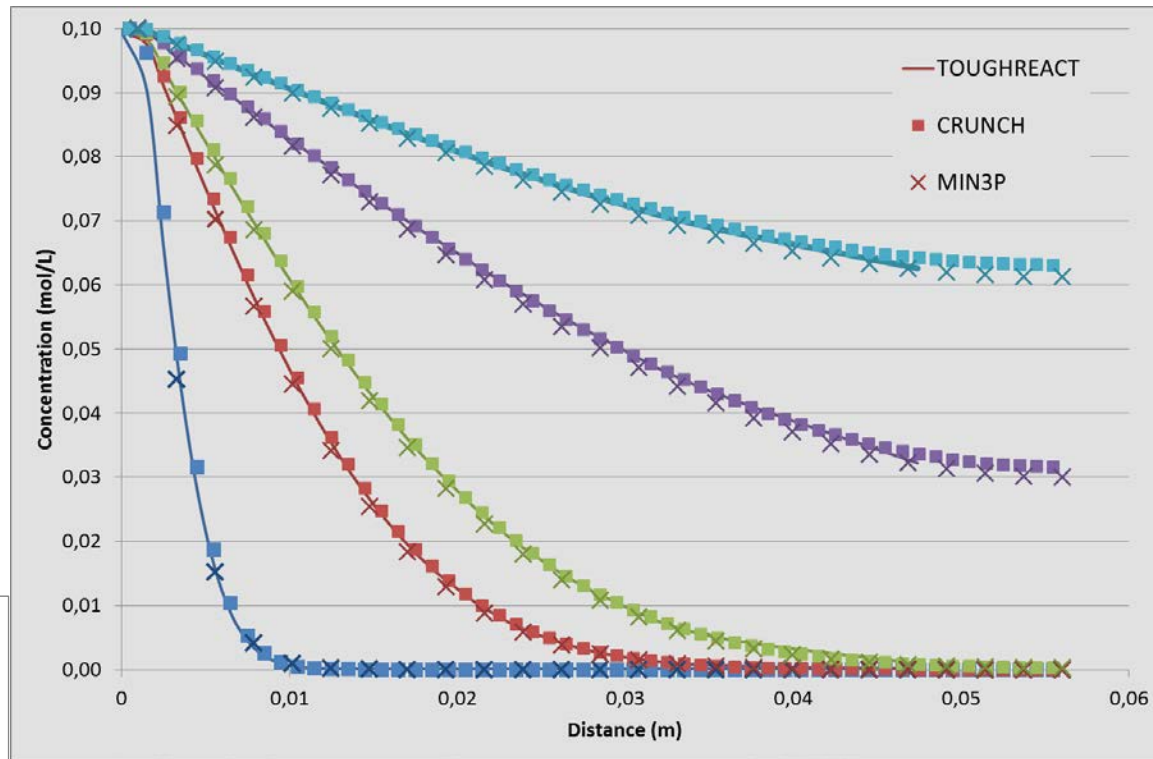
# COMPONENT 2: REACTION TRANSPORT RESULTS AT CONSTANT $S_L$

Making sure the same effective diffusion coefficient is used...

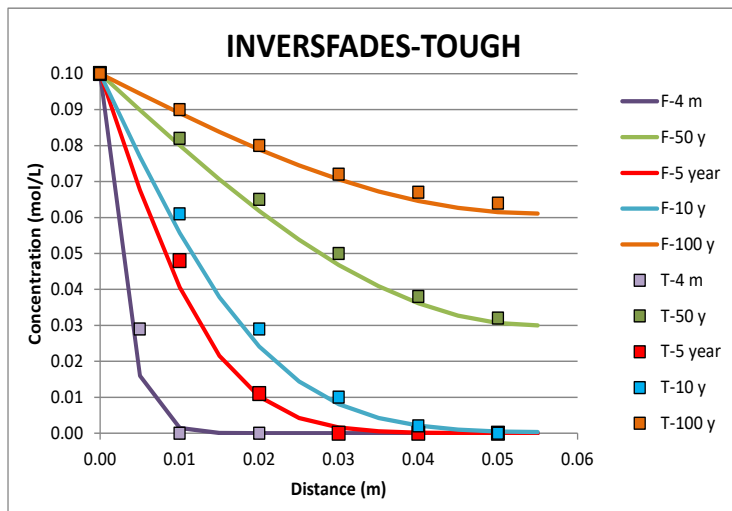
## coupling equation

(Millington-Quirk relationship):

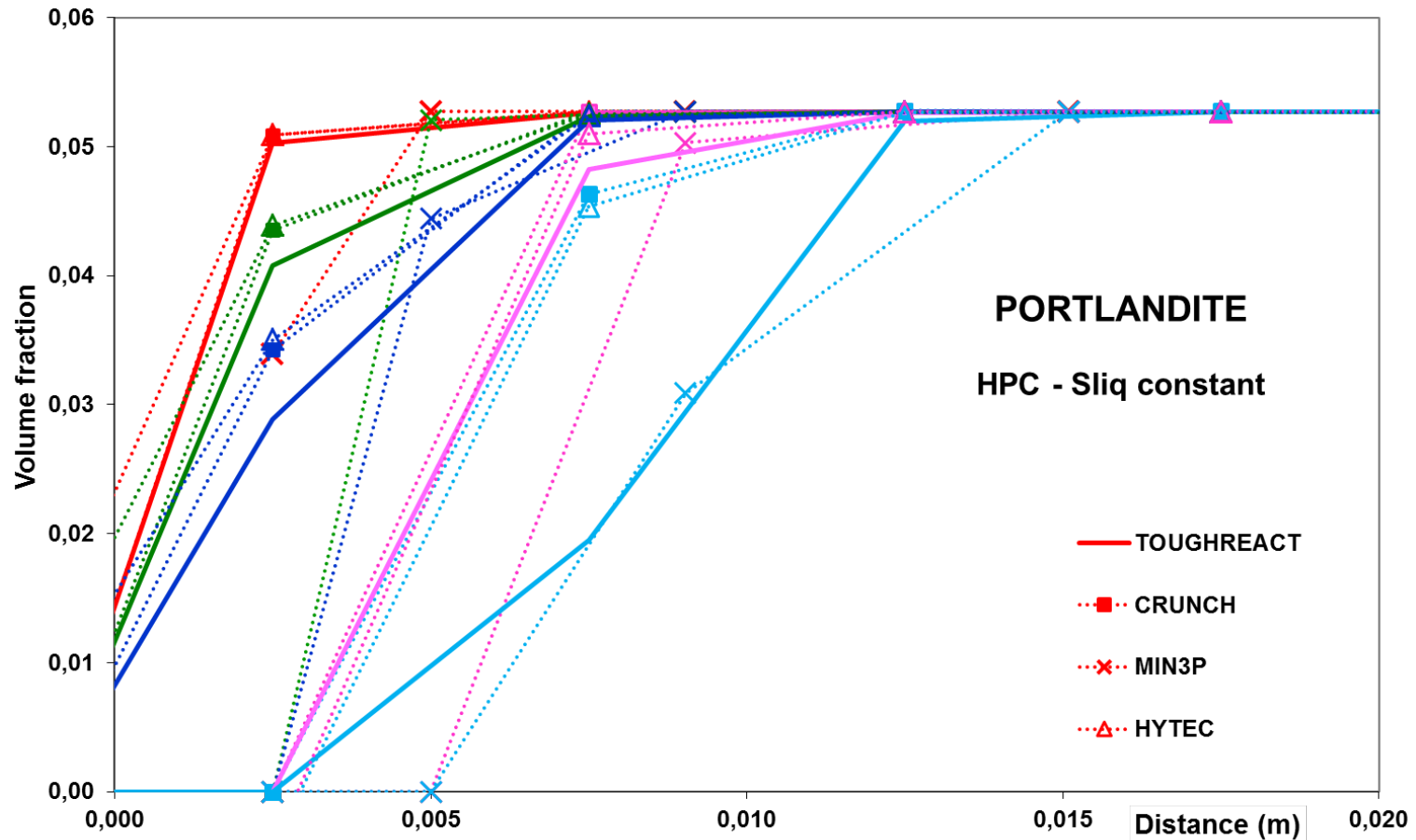
$$D_{eff} = D_0 \omega^a S_l^b$$



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

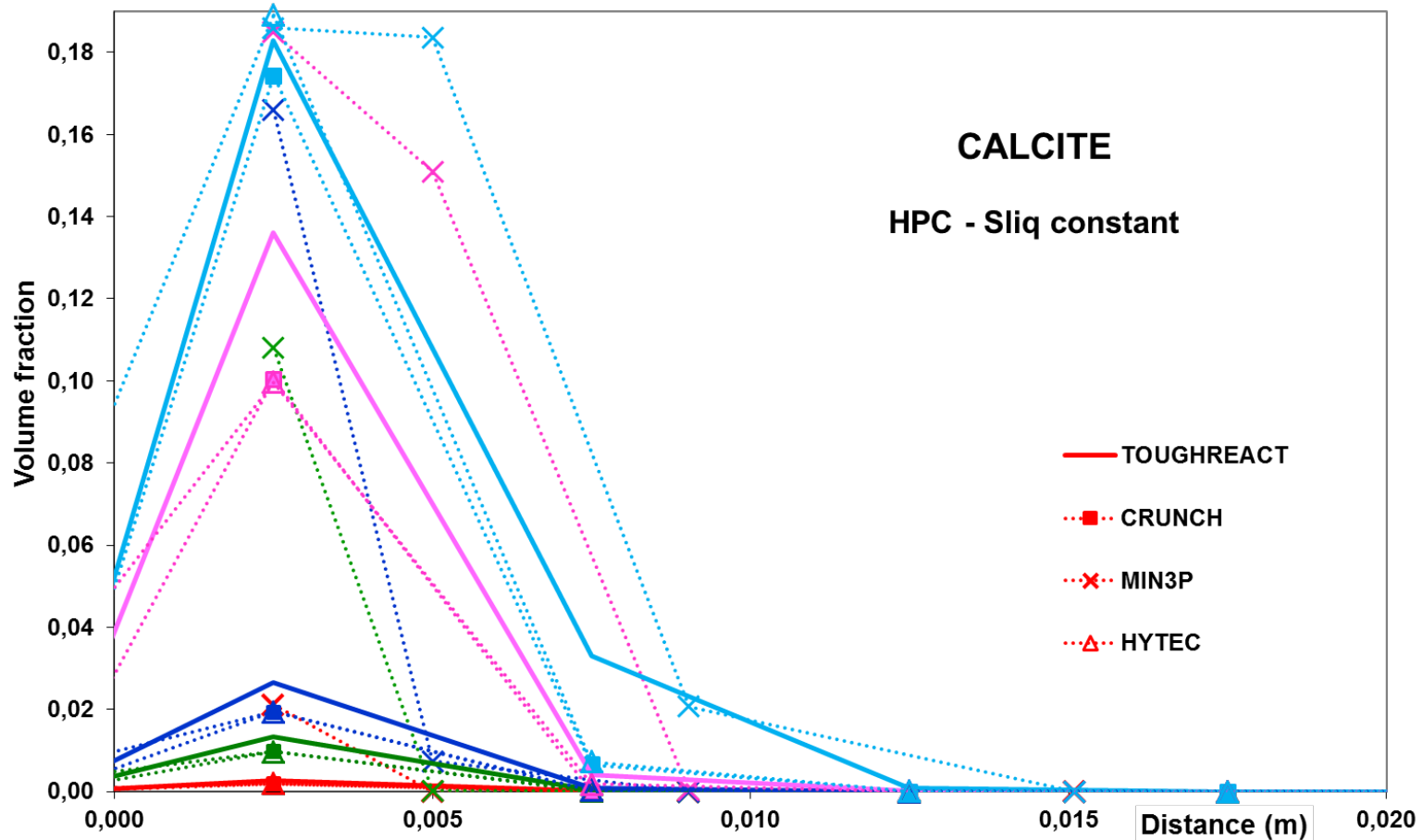


# COMPONENT 2B: CONCRETE CARBONATION AT CONSTANT $S_L$



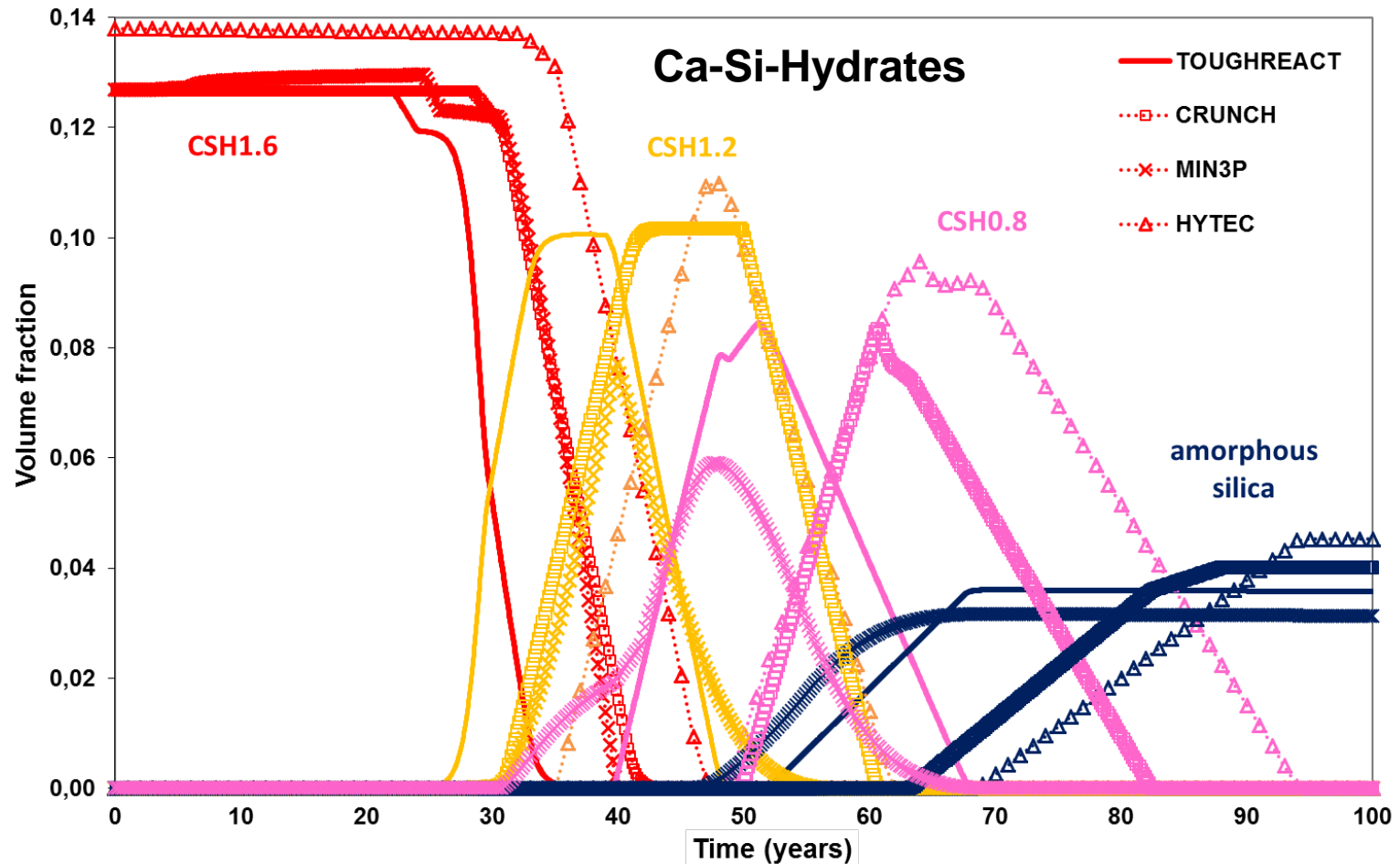
**Carbonation front is similar, but the size of grid cells limits precise comparison**

# COMPONENT 2B: CONCRETE CARBONATION AT CONSTANT $S_L$



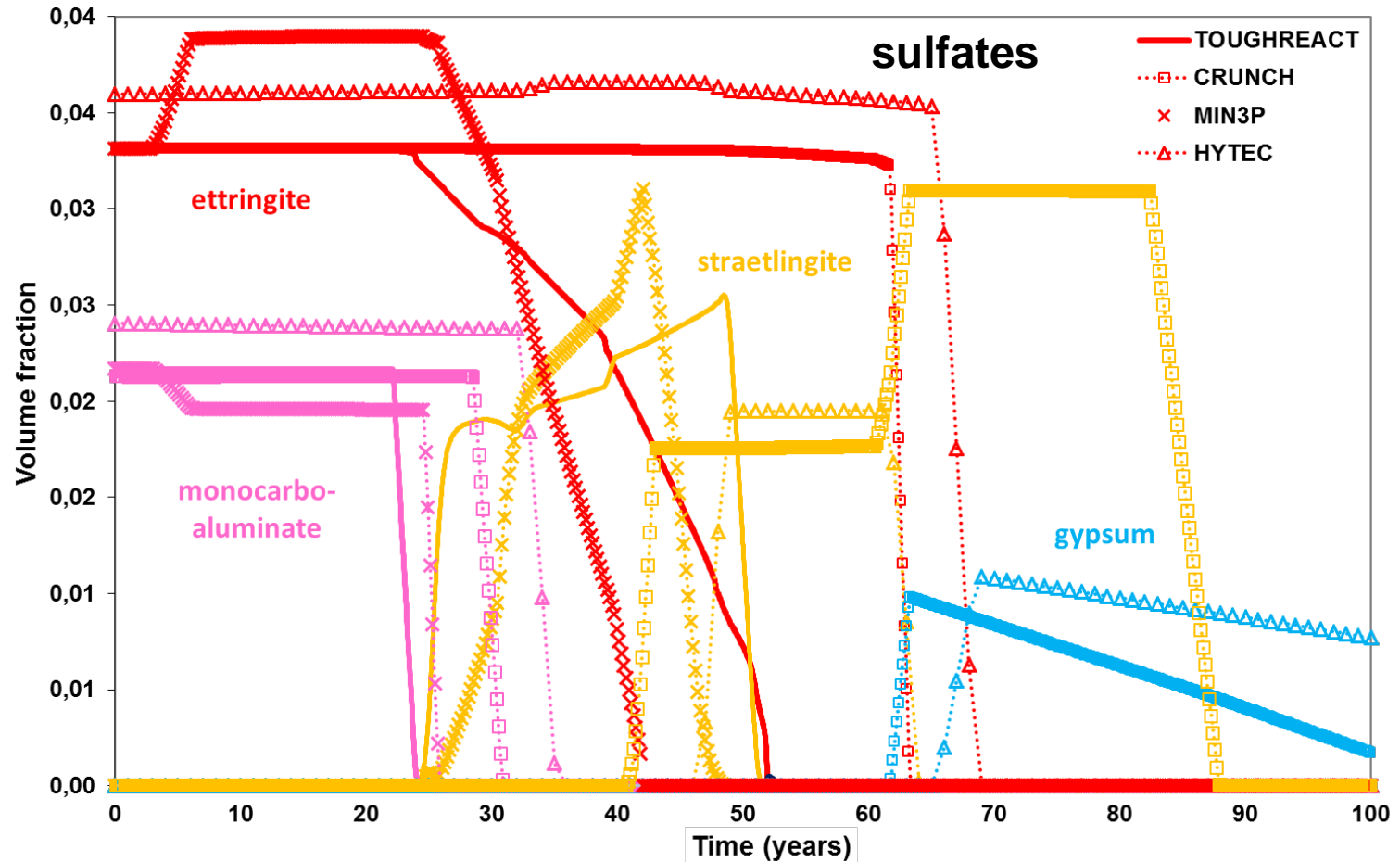
**Calcite precipitation front is similar (MIN3P a little ahead of time/distance)**

# COMPONENT 2B: CONCRETE CARBONATION AT CONSTANT $S_L$



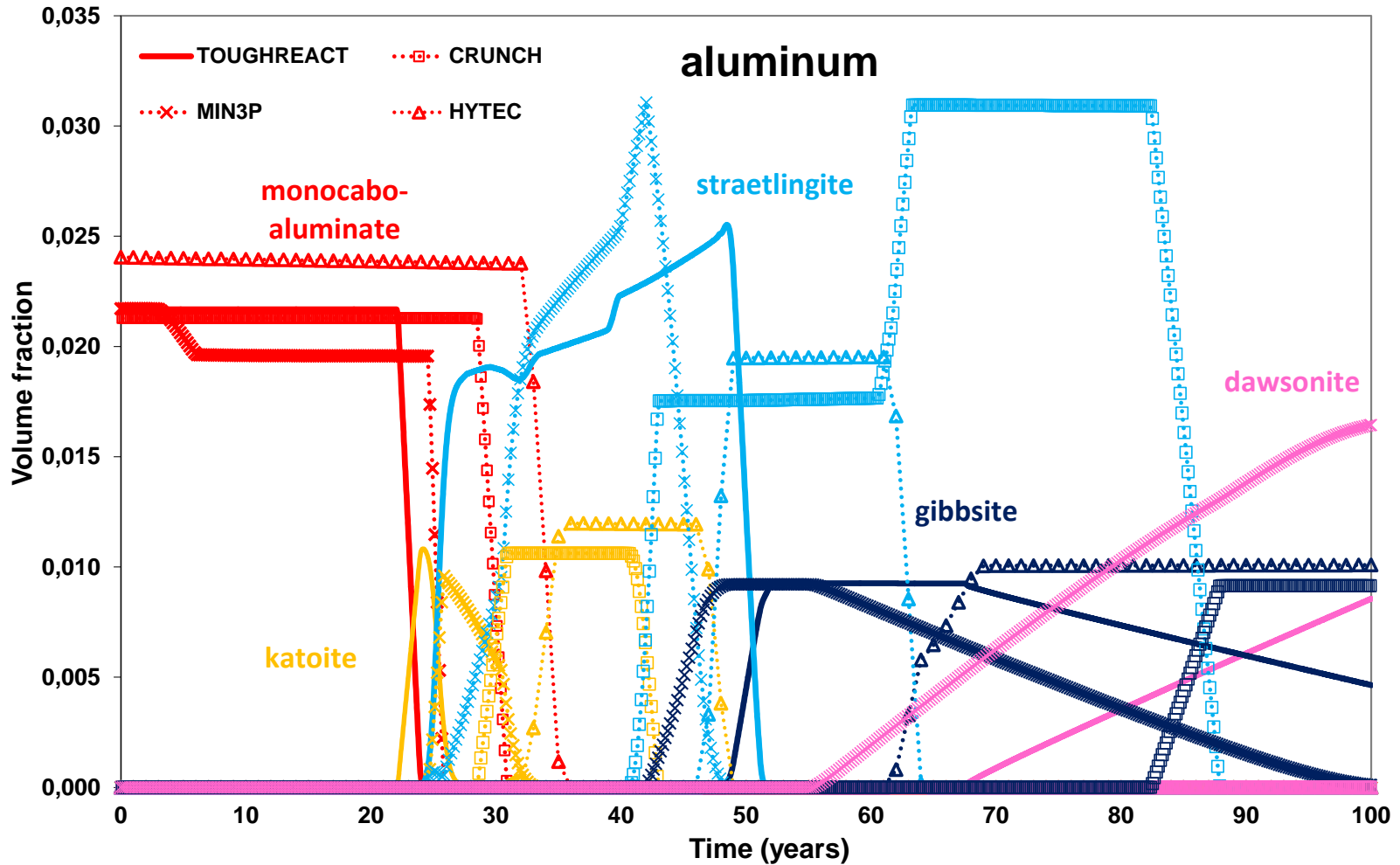
Same mineral paragenesis but timing not exactly the same for all codes

# COMPONENT 2B: CONCRETE CARBONATION AT CONSTANT $S_L$



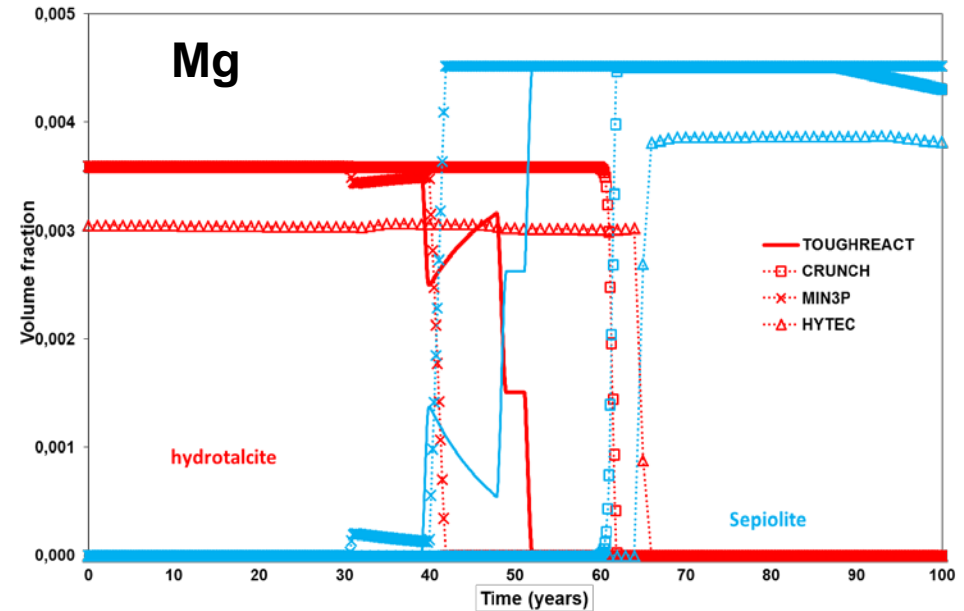
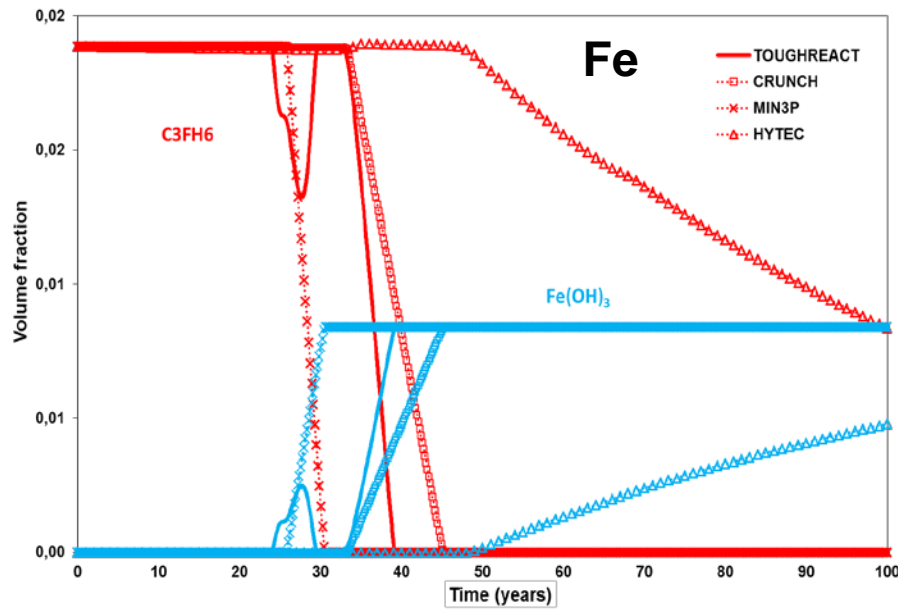
Precipitation of gypsum in the simulation with Crunchflow and Hytec

# COMPONENT 2B: CONCRETE CARBONATION AT CONSTANT $S_L$



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

# COMPONENT 2B: CONCRETE CARBONATION AT CONSTANT $S_L$



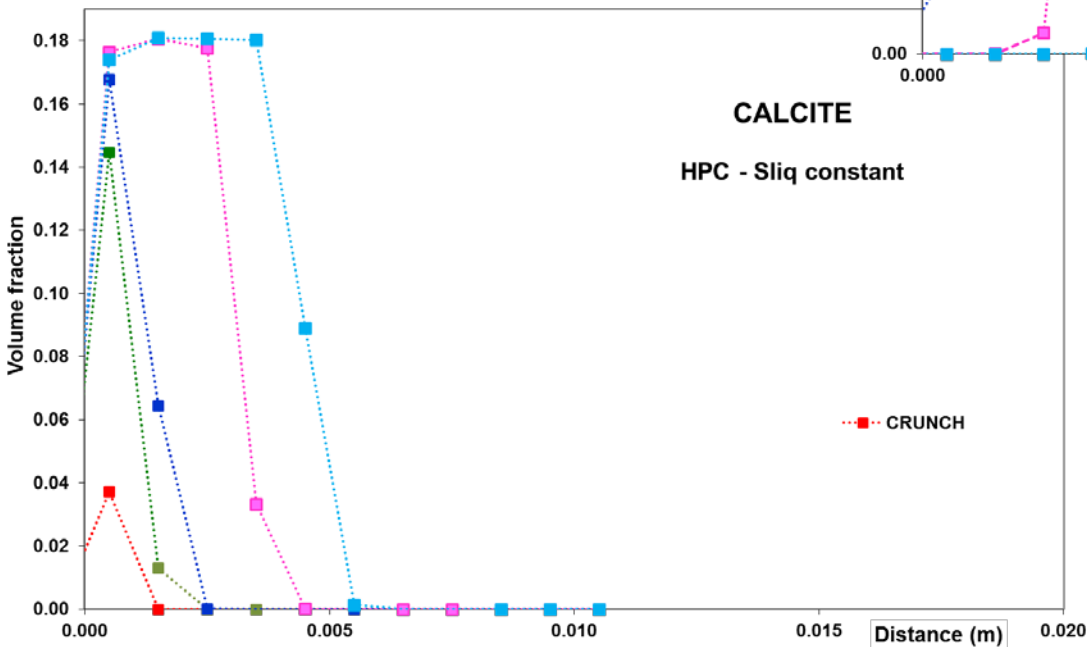
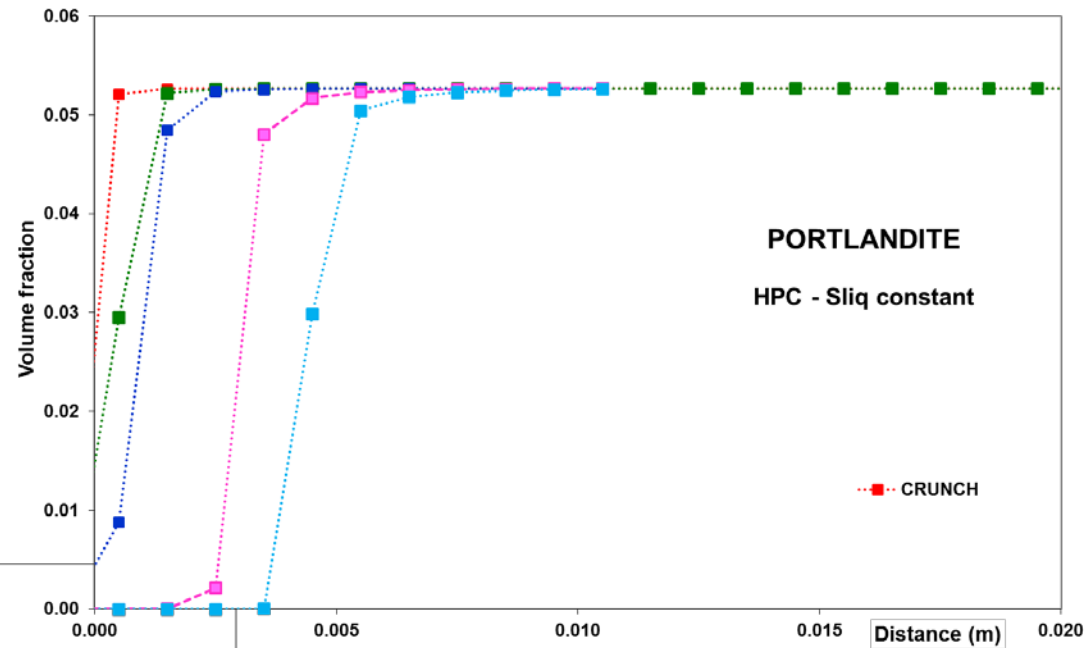
**Same mineral paragenesis but timing not exactly the same for all codes**



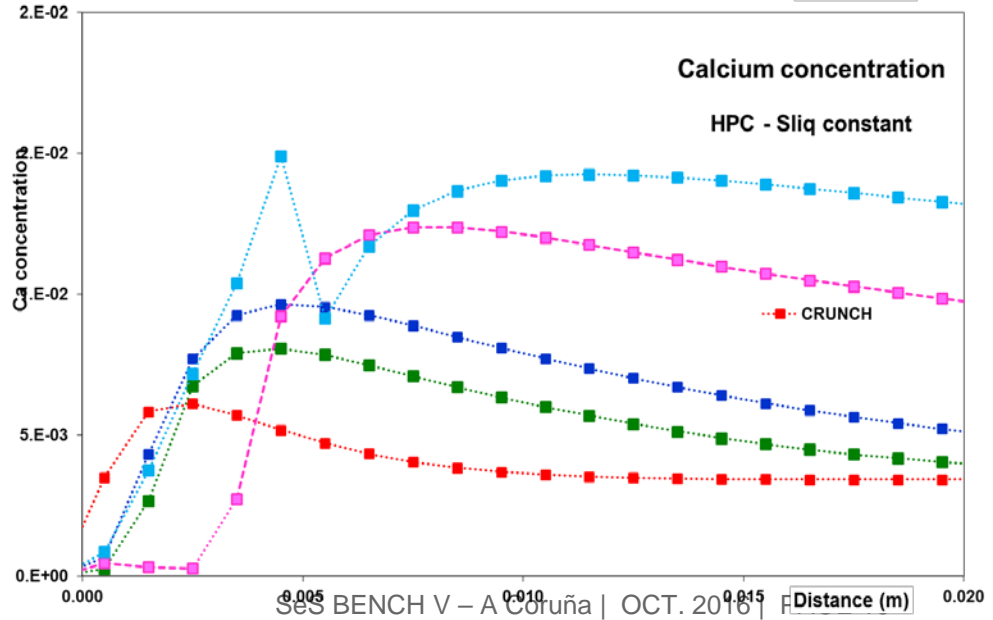
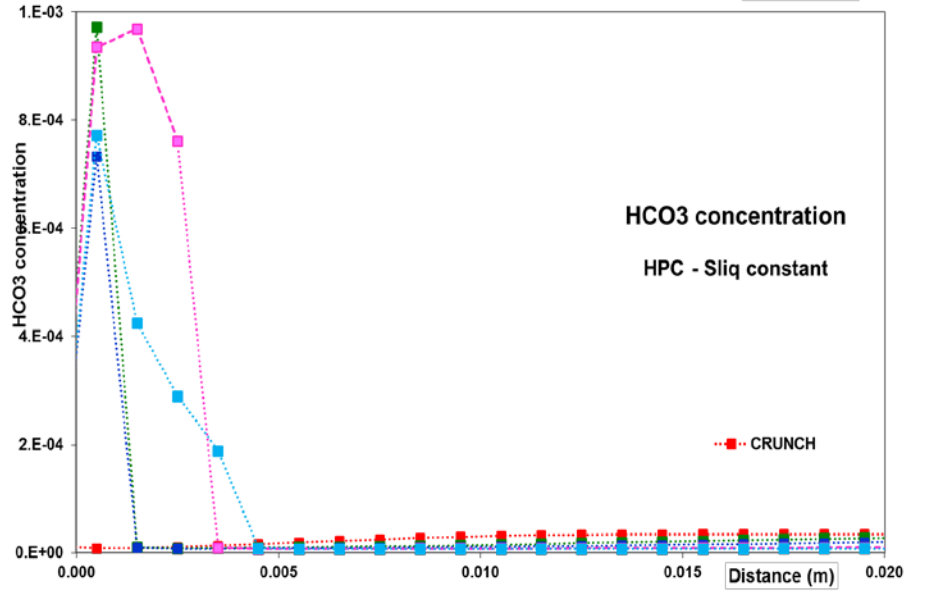
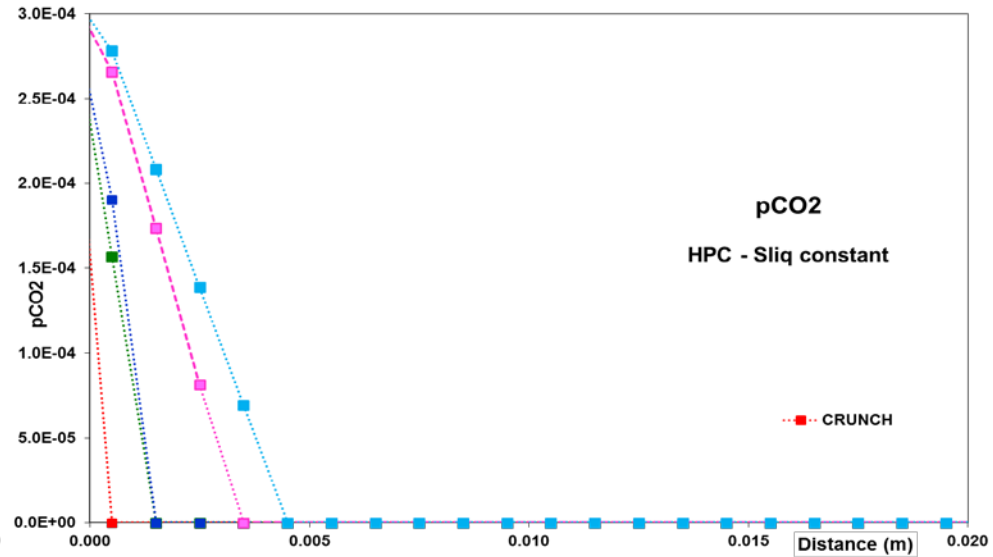
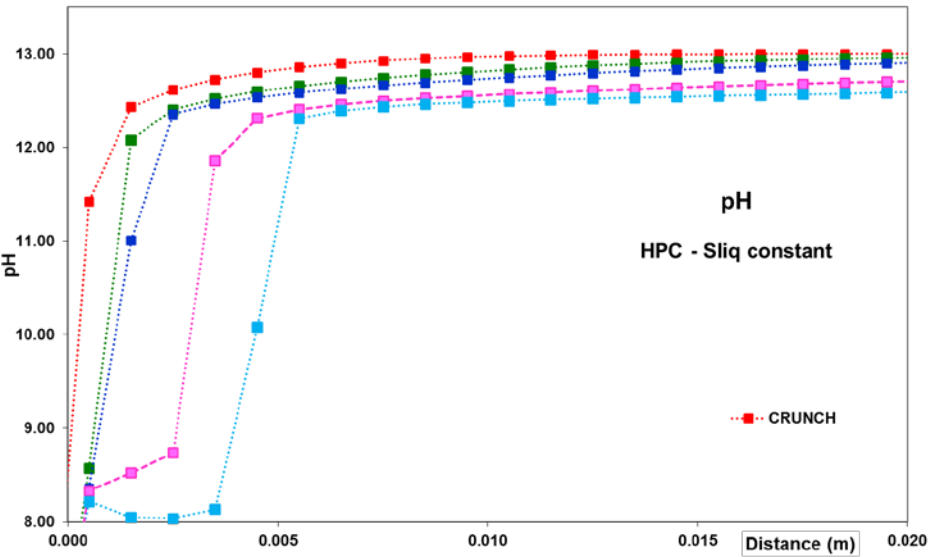
# COMPONENT 2A: PORTLANDITE-CALCITE SYSTEM AT CONSTANT $S_L$

The discrepancies observed in the complex prompted a simpler simulation case (component 2A) with only

Portlandite and Calcite



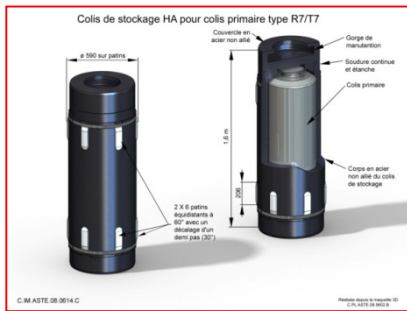
# COMPONENT 2A: PORTLANDITE-CALCITE SYSTEM AT CONSTANT $S_L$



- ✓ Concrete carbonation 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 with simplified chemistry
  
- ✓ Component 3 with fully coupled drying+carbonation only with Toughreact
  
- ✓ New component : variable porosity?

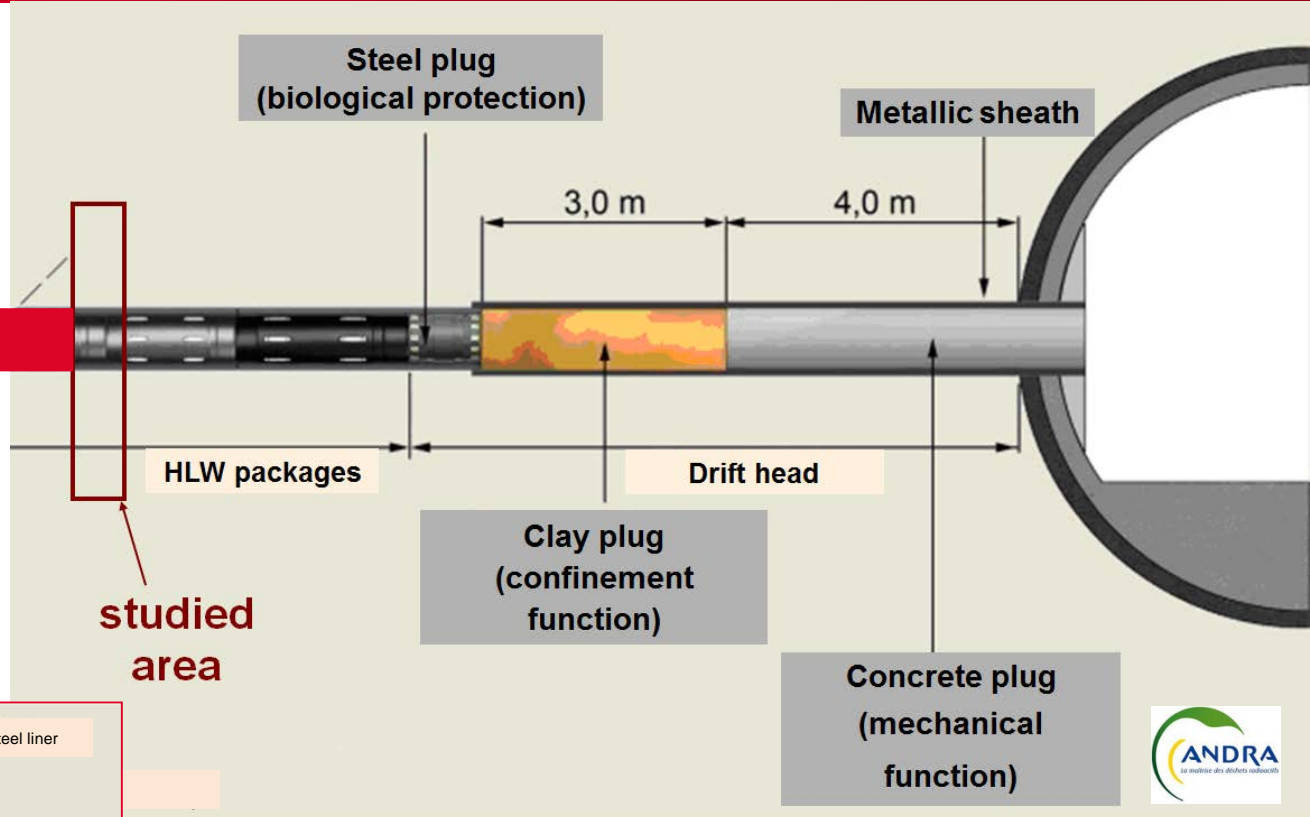
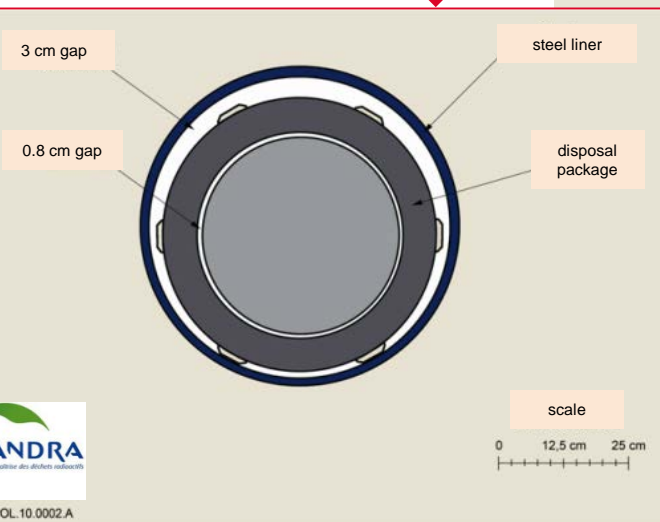
**Glass & steel  
corrosion and  
redox control  
in claystones**

# HLW DISPOSAL CELL



Vitrified waste packages

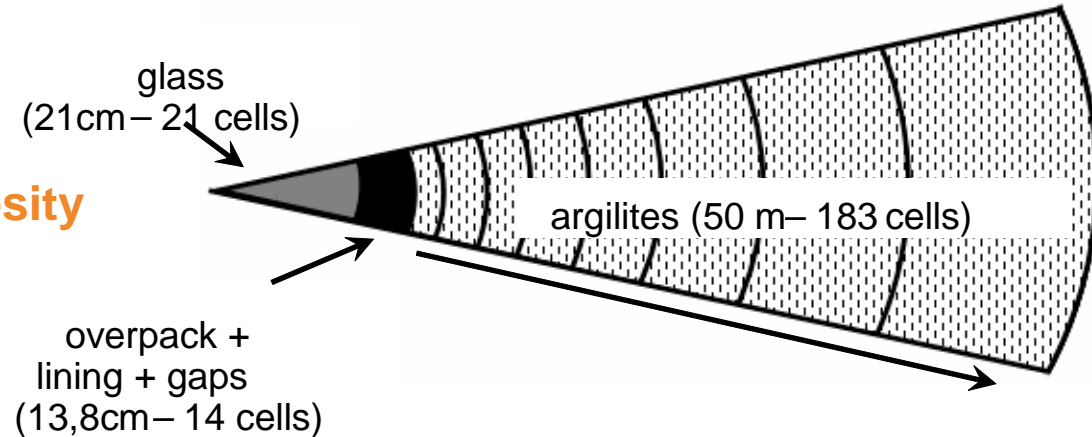
Cross section



- different types of material in physical contact, technological gaps
- **long term calculations of geochemical evolution (100 000 years)**



- 1D radial domain
- transport: diffusion only
- water saturated, constant porosity
- isothermal conditions
- $H_2(g)$  from anoxic corrosion  
 $pH_{2(max)} = 60 \text{ bar}$



- glass  
 $\Phi = 0.42 \text{ m}$ ,  $H = 1 \text{ m}$   
porosity = 0.12
- metallic components  
total thickness = 0,095 m,  
porosity = 0.25
- connected fractured zone  
 $0.4 * \text{excavation diameter} = 0.268 \text{ m}$   
porosity = 0.20;  $D_{\text{eff}}(25^\circ\text{C}) = 5.2 \cdot 10^{-11} \text{ m}^2/\text{s}$
- undisturbed claystone (50 m)  
porosity = 0.18;  $D_{\text{eff}}(25^\circ\text{C}) = 2,6 \cdot 10^{-11} \text{ m}^2/\text{s}$

## Major challenge comes from:

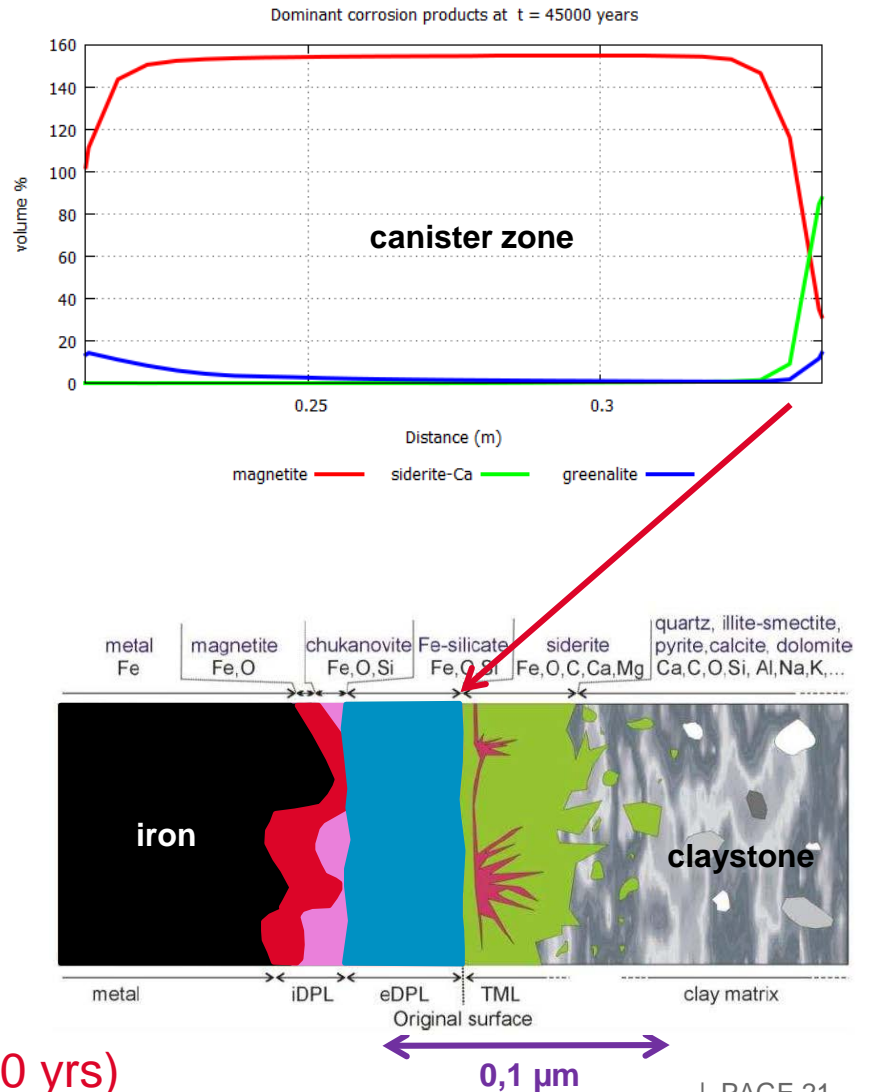
- highly reactive system  
(strong pH and redox perturbation)
- complex geochemical system  
(15 chemical elements, 80 aqueous species, 60 minerals)

## Component 1: iron corrosion only (45 000 yrs)

- magnetite, Ca-siderite, and greenalite dominate  
(oxide) (carbonate) (silicate)
- also smaller amounts of aluminosilicates  
(nontronites and saponites)
- POROSITY CLOGGING (not taken explicitly into account)
- modeling vs. experimental results  
iron/claystone at 90°C for 1 year
- small amount of magnetite
- siderite(-Ca), Fe-silicates

→ more phenomenological model for corrosion

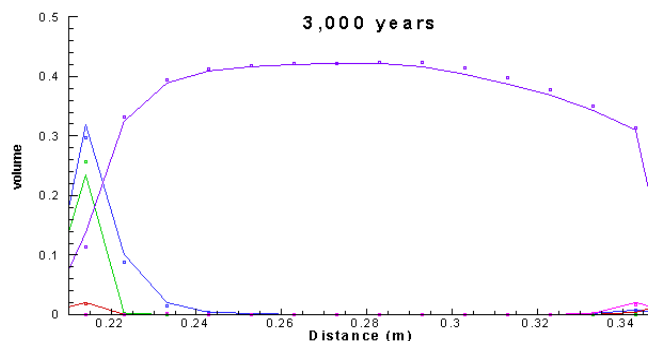
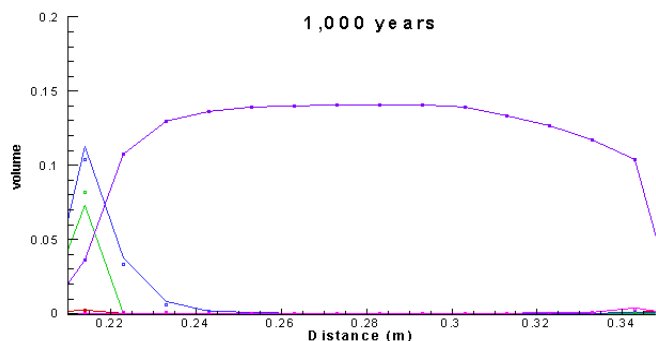
## Component 2: iron corrosion + glass alteration (100 000 yrs)



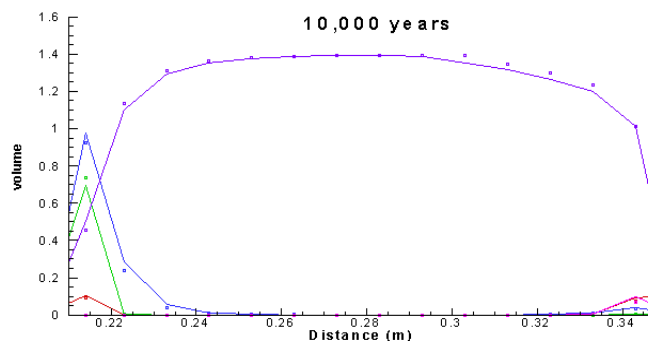
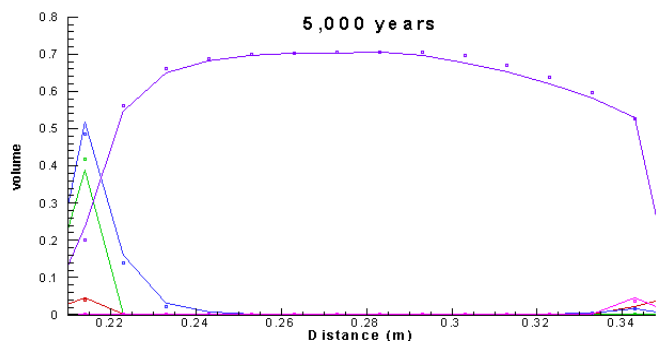


# COMPONENT 1: RESULTS IN THE BASE CASE

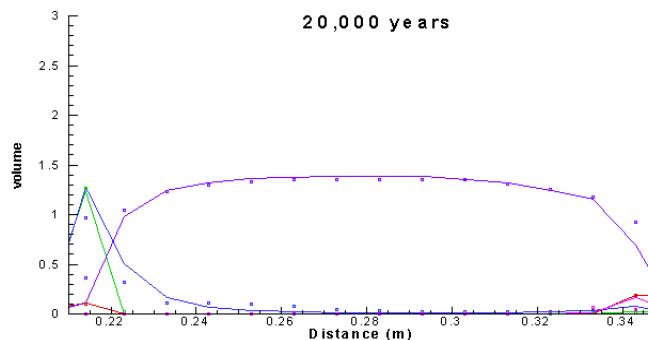
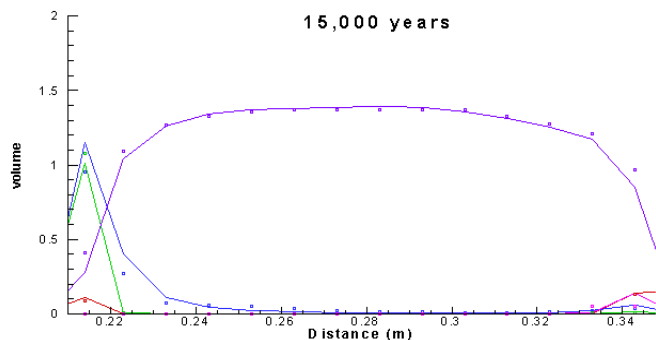
**ONLY 2 CODES** : MIN3P-Crunchflow (a very good agreement is obtained!) ...



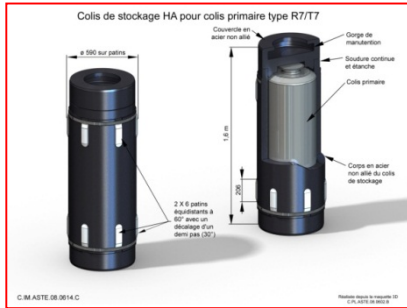
**in the iron zone**



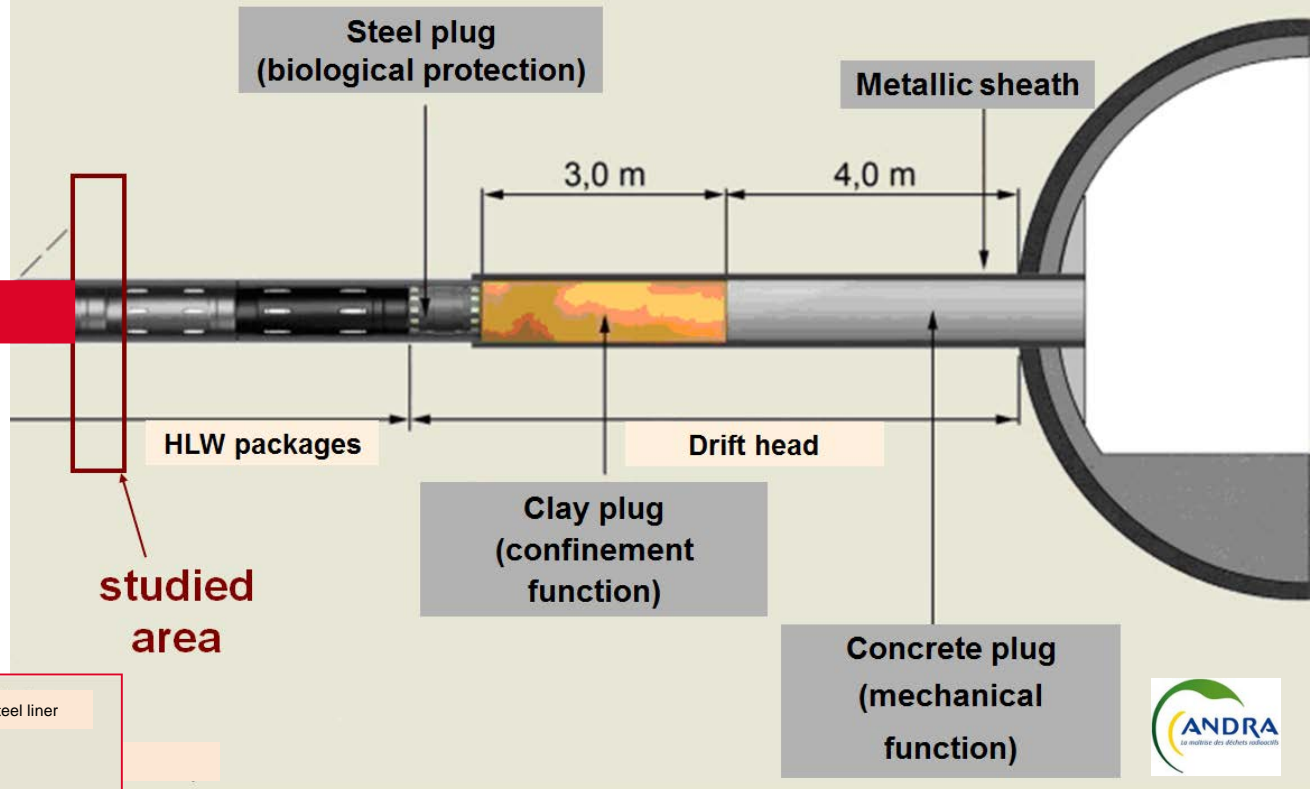
- Daphnite\_14A - crunchflow
- Fe-Saponite-Na - crunchflow
- Greenalite - crunchflow
- Magnetite,beta - crunchflow
- Pyrrhotite-alpha - crunchflow
- - Daphnite\_14A - MIN 3P
- - Greenalite - MIN 3P
- - Fe-Saponite-Na - MIN 3P
- - Pyrrhotite-alpha - MIN 3P
- - Magnetite,beta - MIN 3P



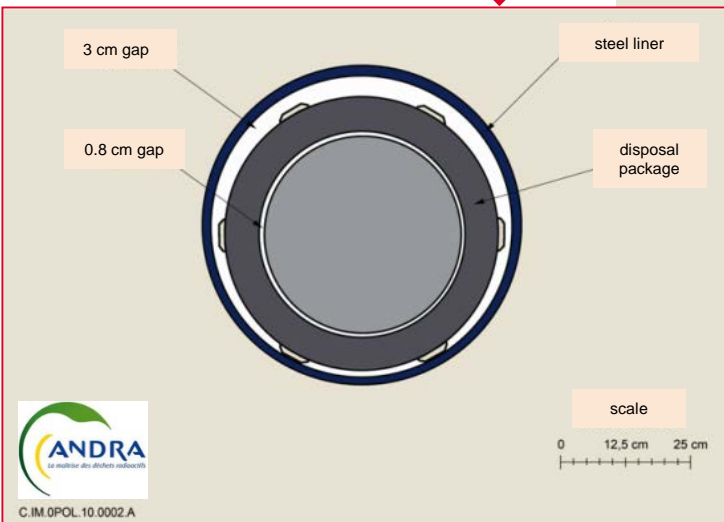
# CORROSION IN HLW DISPOSAL CELL



Vitrified waste packages



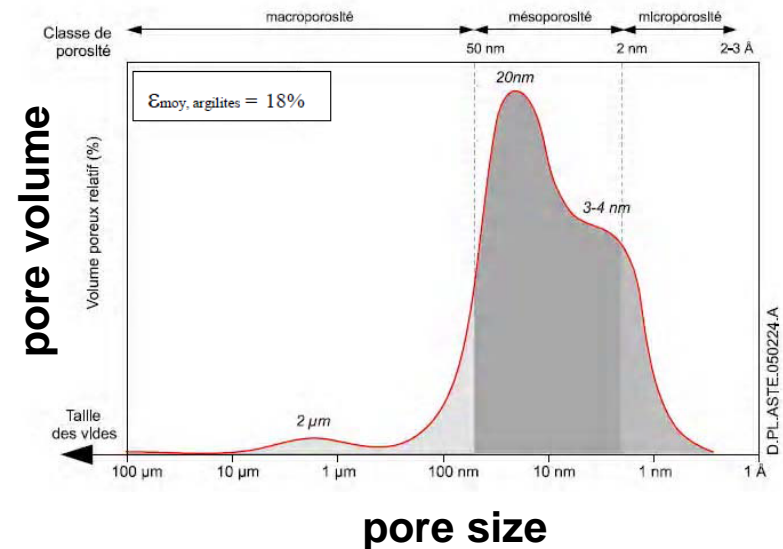
Cross section



- production of hydrogen: how reactive is it?
- redox in claystones: who is in control?
- how is corrosion represented in reactive transport codes?

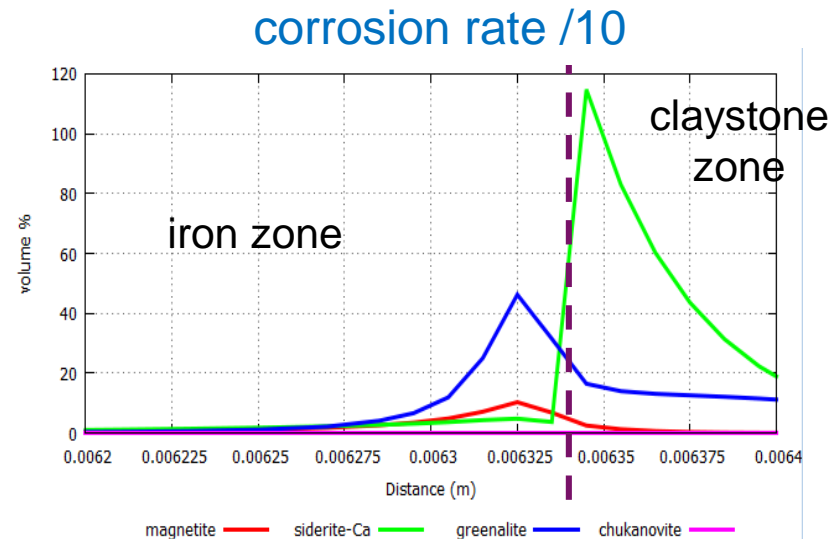
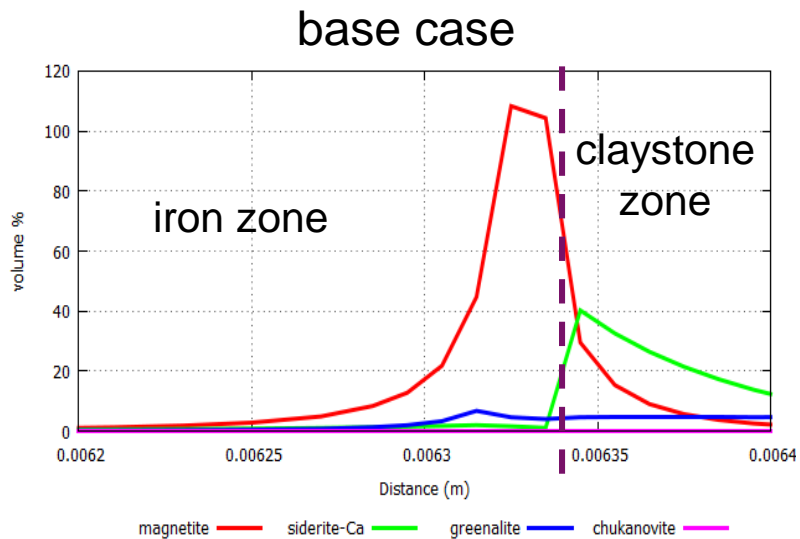
- reactivity of  $H_2$  in claystones  
(in tiny 20 nm connected pores)
  - only at interfaces in repository
  - redox control in claystones?
  - RN sorption/migration?
  - porosity clogging

- discussion: coupling of electrochemical corrosion reactions with reactive transport codes



## ✓ Corrosion in reactive transport codes

- ✓ changes in pH and Eh occur through:

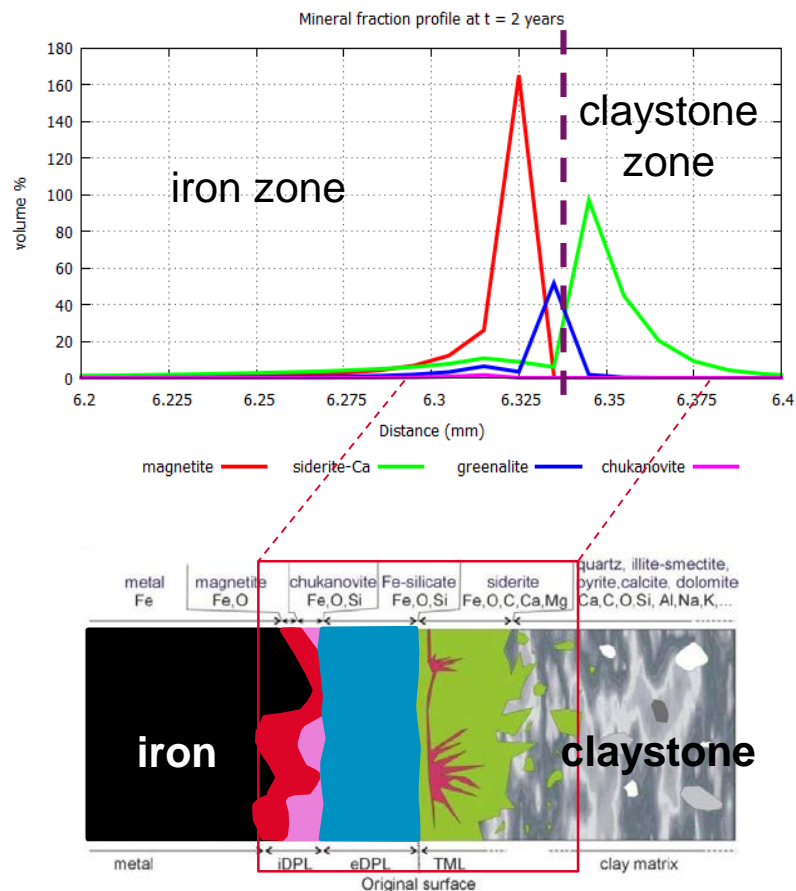


# STEEL CORROSION “GEOCHEMICAL” REACTION

... but the paragenesis of secondary minerals is not predicted correctly

To match the mineralogical paragenesis, we have to modify:

- (very low) diffusional properties in the corroded layer
- (high) magnetite precipitation rate



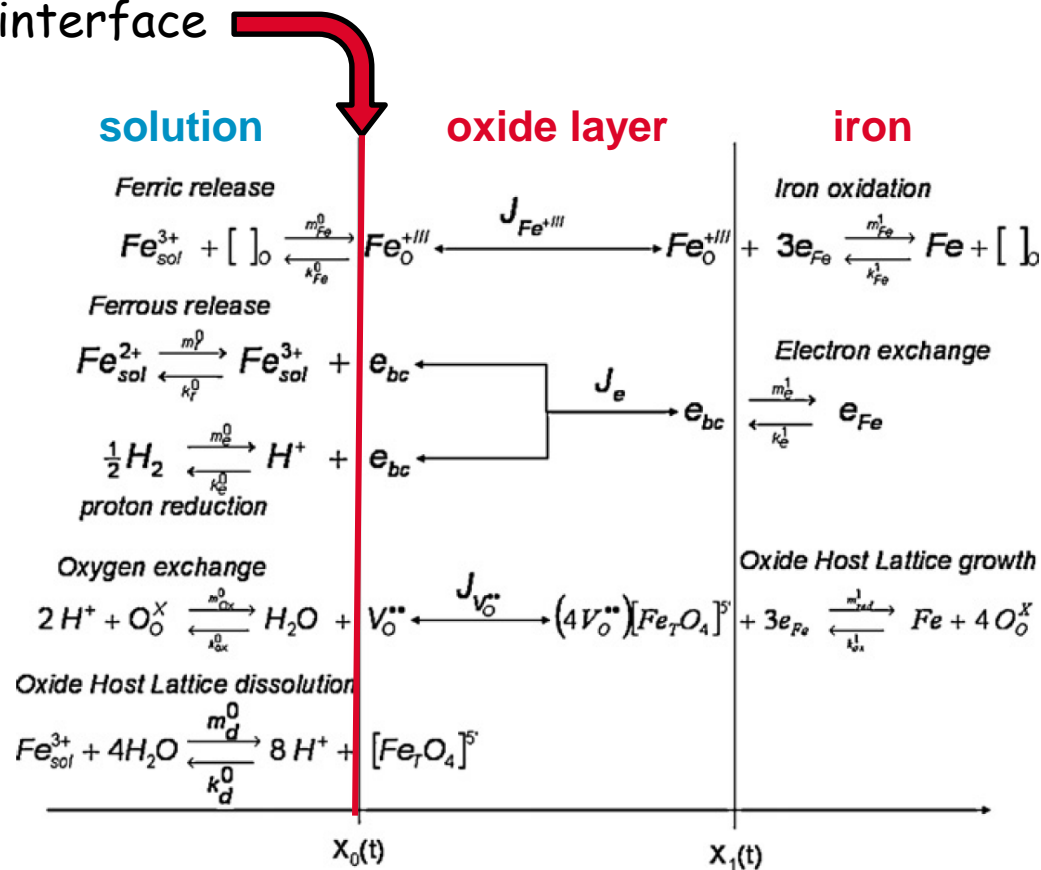
from Schlegel et al. 2014

## Corrosion: an electrochemical model

✓ redox reactions occurring at the interface

✓ non-equilibrium reactions involving electrons in the conduction band

✓ corrosion generates fluxes of  $Fe^{2+}$ ,  $Fe^{3+}$ ,  $H_2$ ,  $H^+$ , ...



Diffusion Poisson Coupled Model (DPCM)  
from Bataillon et al. *Electrochem. Acta* 2010

- ✓ Coupling of electrochemical corrosion reactions with reactive transport codes:
  - ✓ use elemental fluxes (Fe, H<sub>2</sub>)?
  - ✓ use mineral reaction rates (corrosion and oxide layer precipitation/dissolution)?
  - ✓ use fluxes for Fe<sup>2+</sup> and Fe<sup>3+</sup> and aqueous kinetics?



**THANK YOU FOR YOUR ATTENTION**

Commissariat à l'énergie atomique et aux énergies alternatives  
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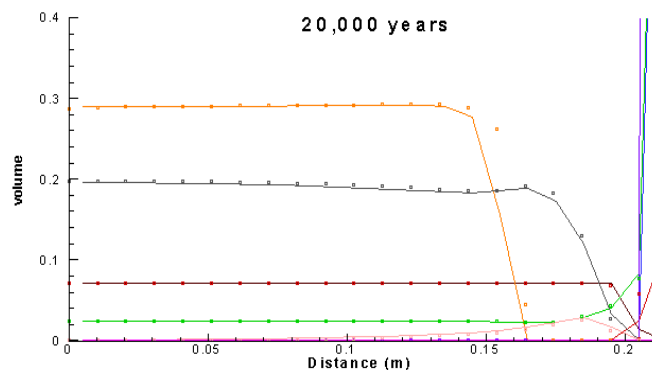
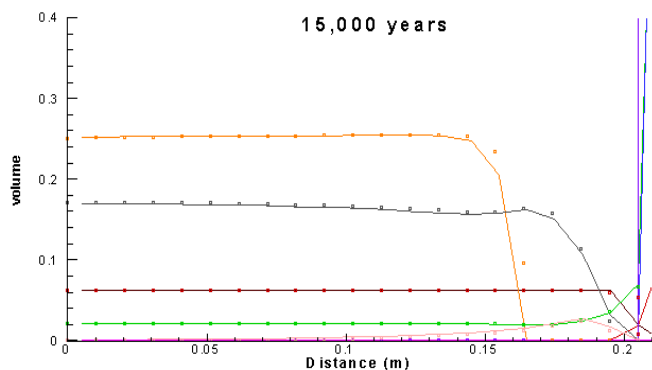
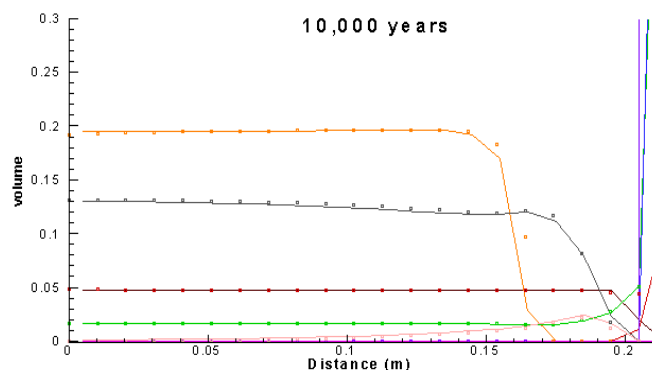
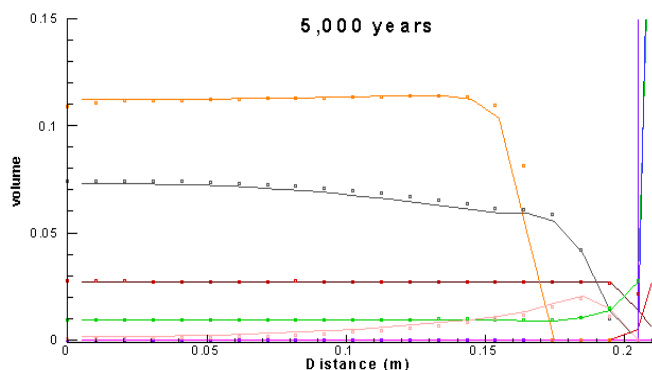
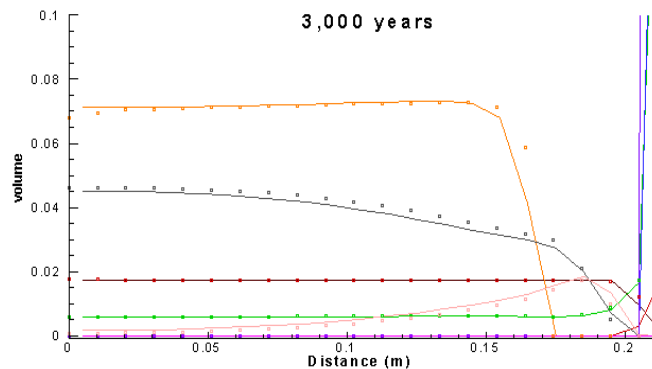
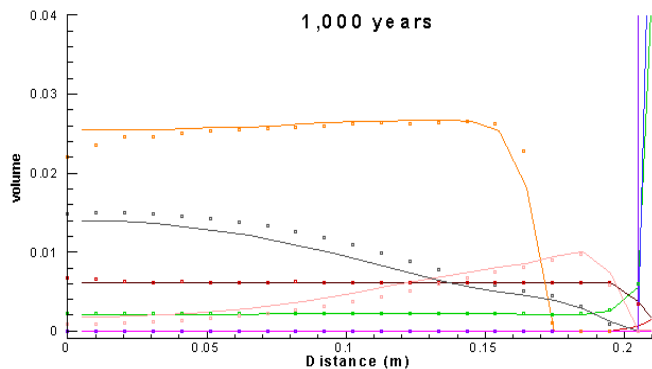
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Direction de l'Energie Nucléaire  
Département des Technologies  
Nucléaires  
Service de Modélisation des Transferts  
et de Mesures Nucléaires

**Update on  
glass/iron/clay  
benchmark**

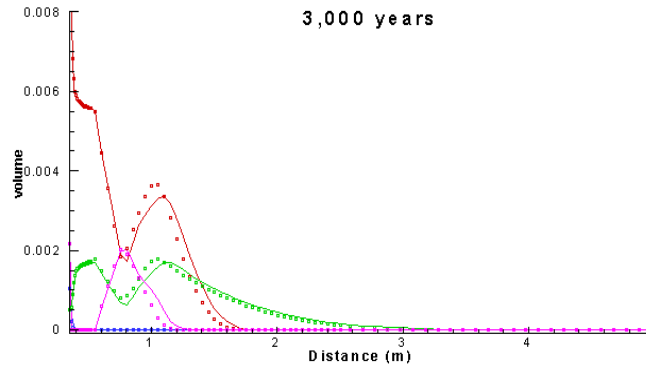
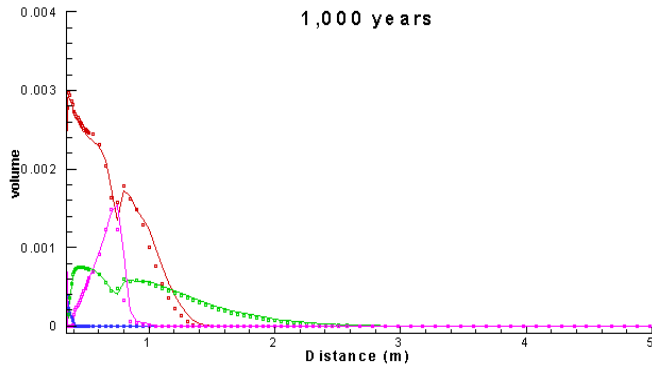
# RESULTS IN THE BASE CASE (3)

**in the glass zone**



- Calcite - crunchflow
- Chalcedony - crunchflow
- Daphnite\_14A - crunchflow
- Fe-Saponite-Na - crunchflow
- Fe-MontmorilloniteNa - crunchflow
- Greenalite - crunchflow
- Illite-FeII - crunchflow
- Magnetite,beta - crunchflow
- Pyrrhotite-alpha - crunchflow
- Daphnite\_14A - MIN 3P
- Greenalite - MIN 3P
- Fe-Saponite-Na - MIN 3P
- Pyrrhotite-alpha - MIN 3P
- Magnetite,beta - MIN 3P
- Chalcedony - MIN 3P
- Fe-MontmorilloniteNa - MIN 3P
- Calcite - MIN 3P
- Illite-FeII - MIN 3P

# RESULTS IN THE BASE CASE (4)



in the clay zone

- Daphnite\_14A - crunchflow
- Fe-Saponite-Na - crunchflow
- Greenalite - crunchflow
- Pyrrhotite-alpha - crunchflow
- - - Daphnite\_14A - MIN3P
- - - Greenalite - MIN3P
- - - Fe-Saponite-Na - MIN3P
- - - Pyrrhotite-alpha - MIN3P

