

# 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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# 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)

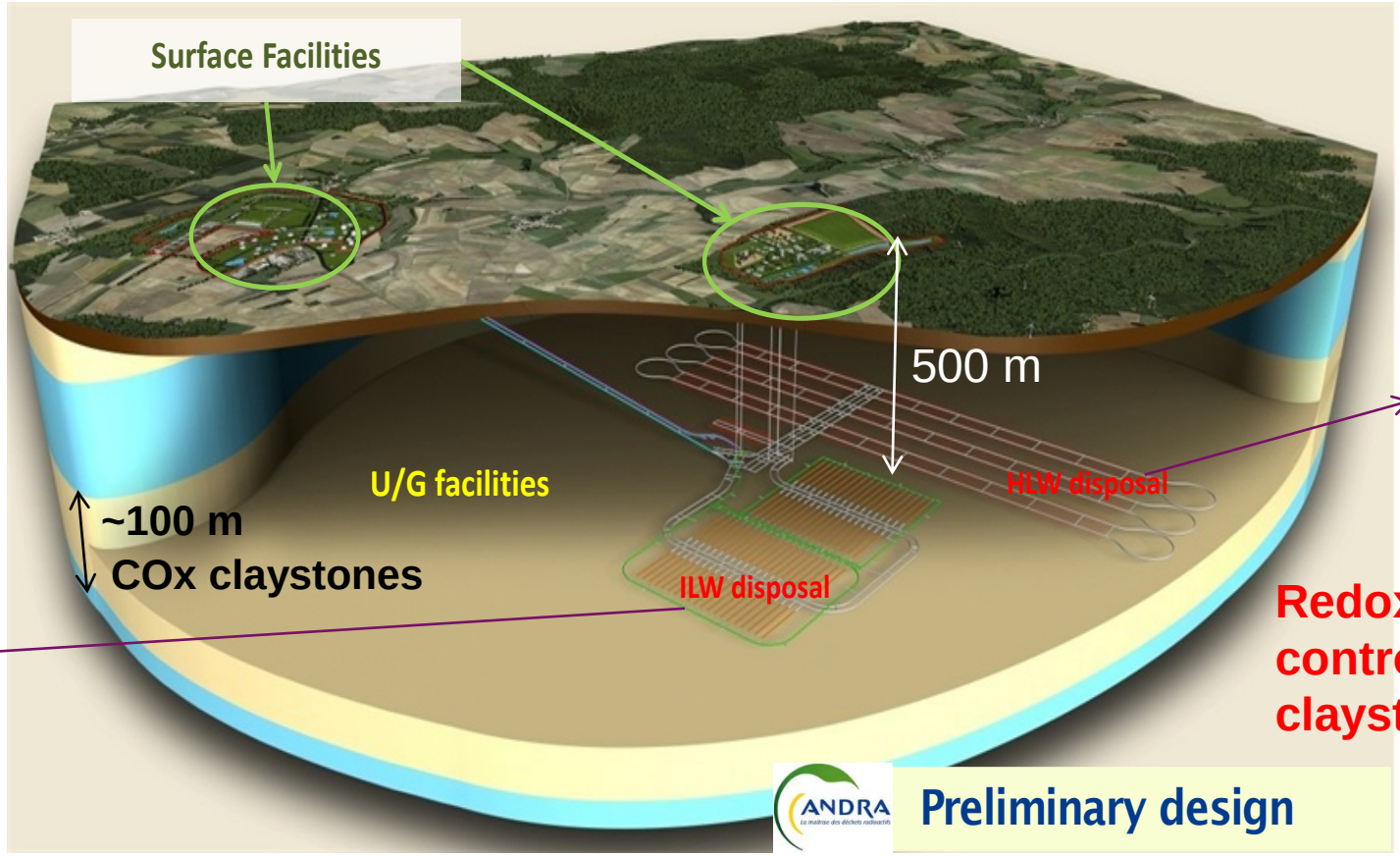
B. Cochepin, I. Munier

Andra (French Radioactive Waste Management Agency)

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

# DISPOSAL CONCEPT IN A CLAYSTONE FORMATION

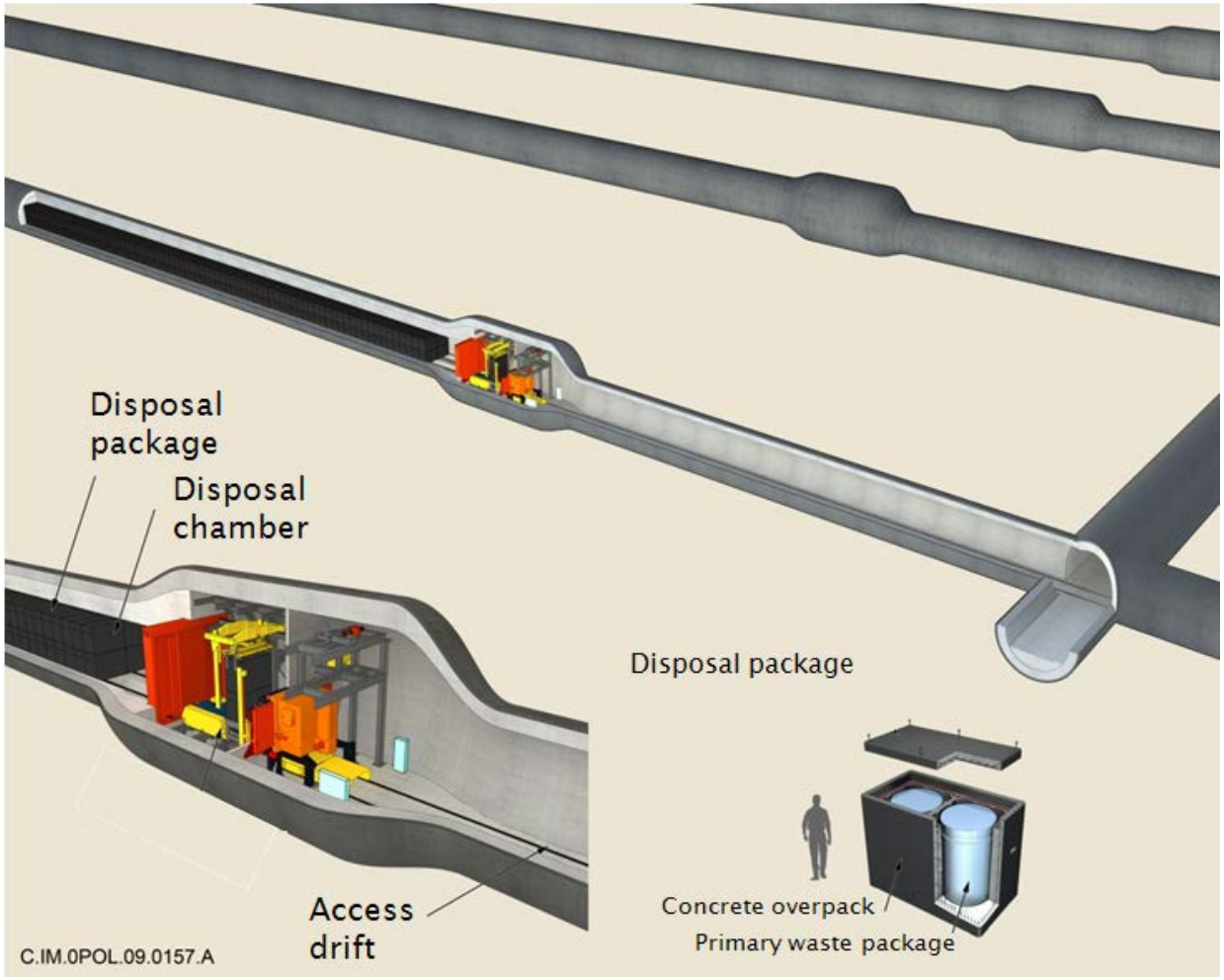
## Current design of deep underground repository for high and intermediate level long-lived waste



# Update of the atmospheric concrete carbonation benchmark

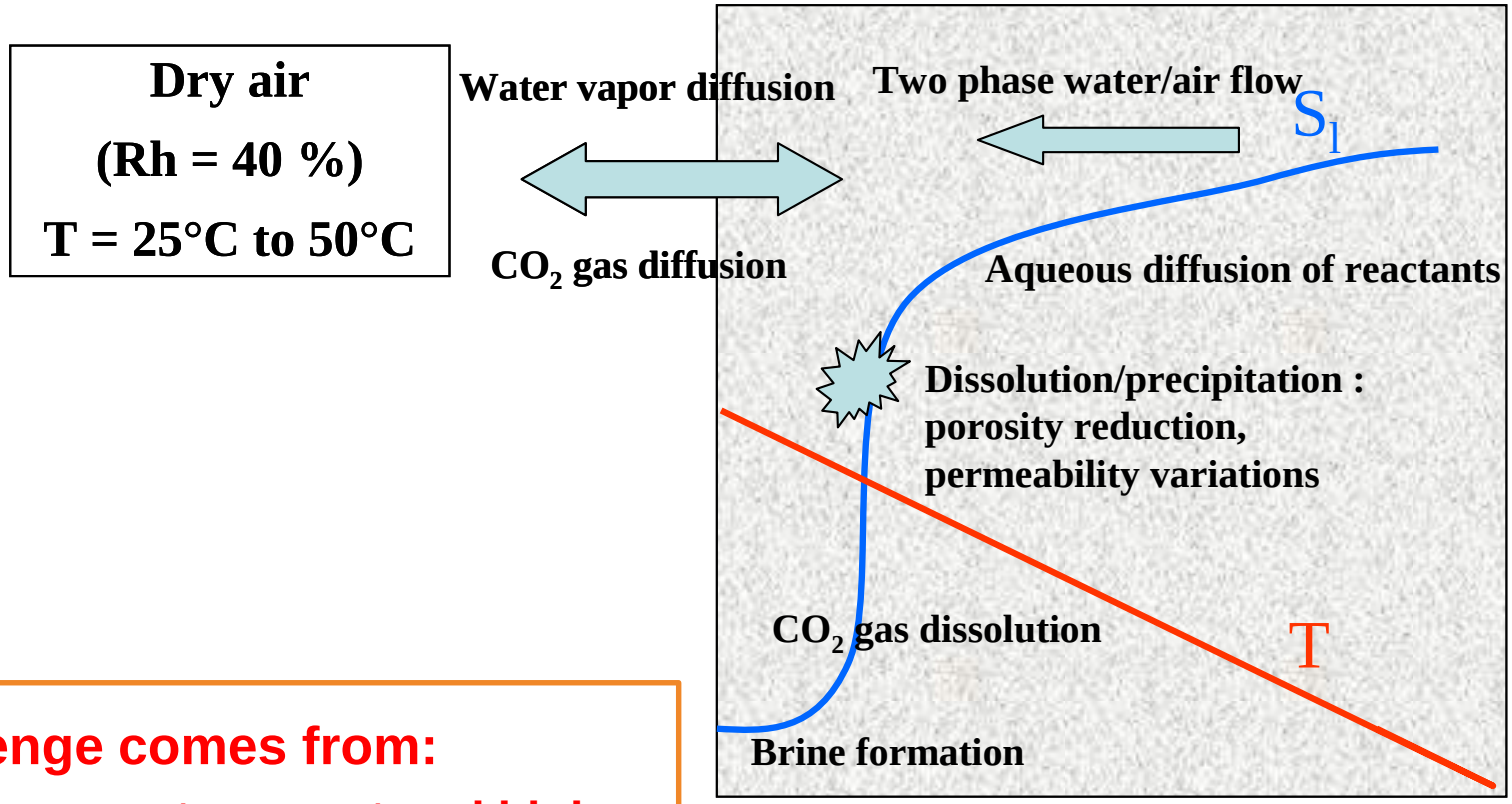
# DESIGN: ILLW CELLS, SHAFTS (AND SEALS), ILLW DISPOSAL OVERPACK

## Atmospheric carbonation of overpack during the operating period




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

# DRYING AND CARBONATION PROCESSES OF ILLW OVERPACK

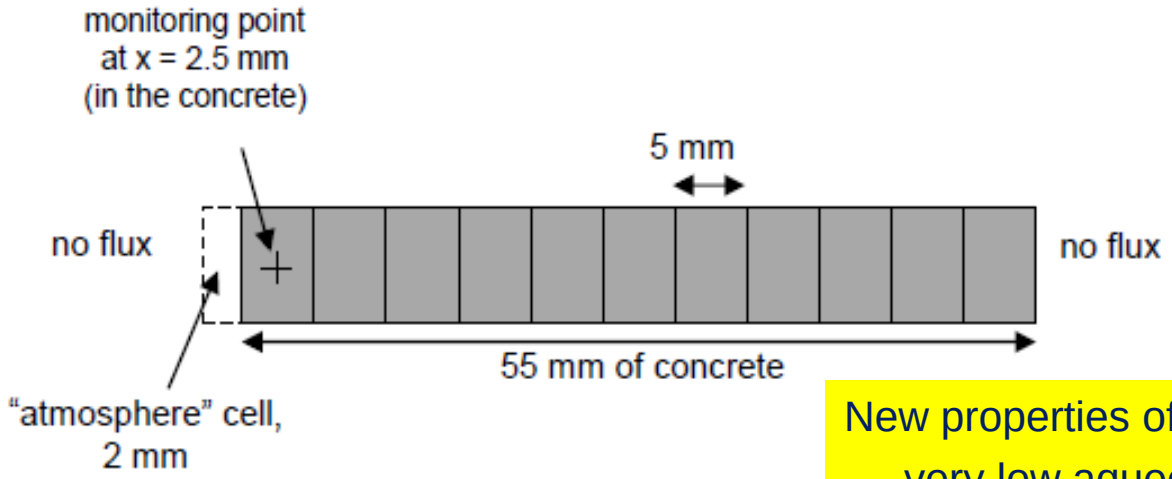



**Major challenge comes from:**

- **$CO_2$ 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 ??

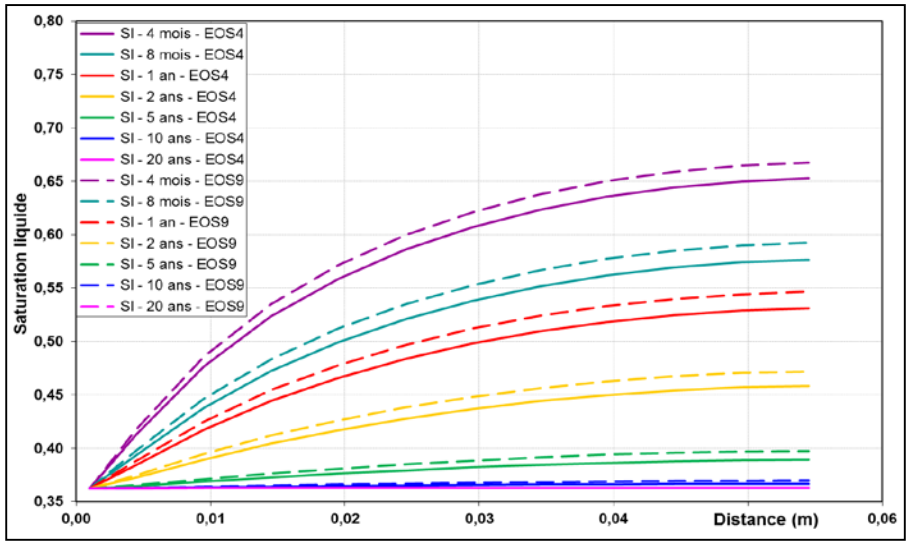
Drying with Richards’ equation :

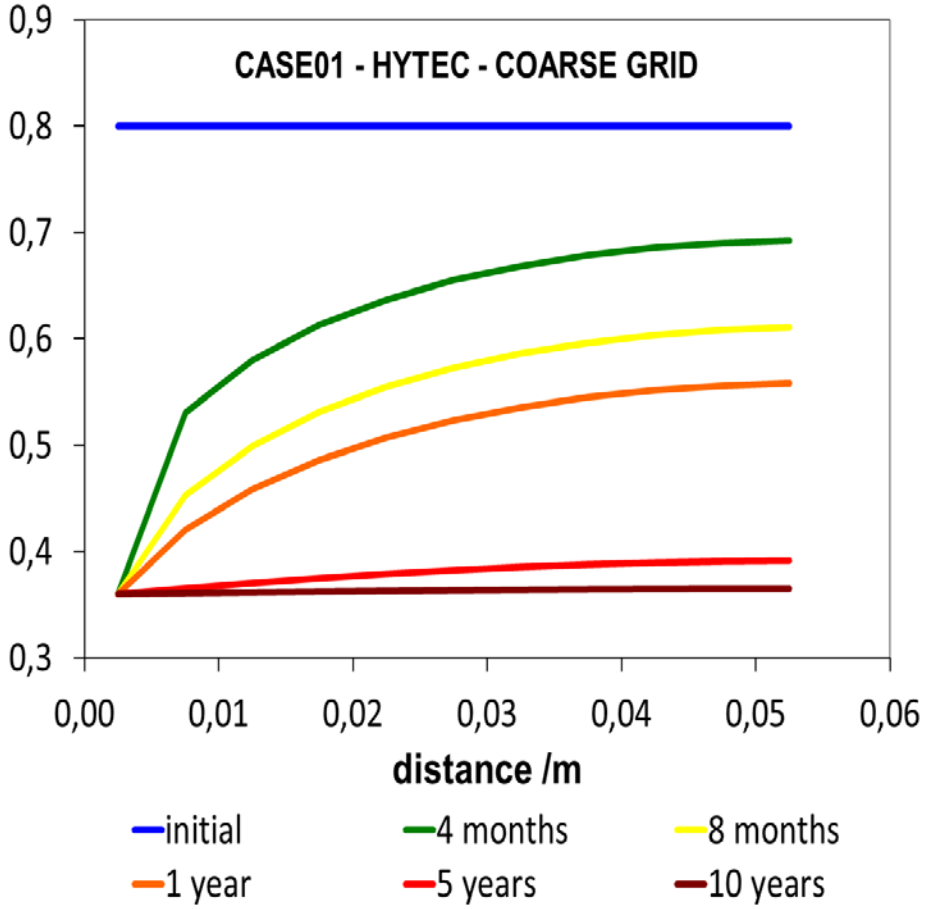
MIN3P (S. Béa, CONICET ; U. Mayer, UBC)

HYTEC (J. Corvisier, Mines Paristech)

Crunchflow (CEA + C. Steefel, LBNL)

# COMPONENT 1: DRYING RESULTS




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

**Hytec (Richards' equation)**

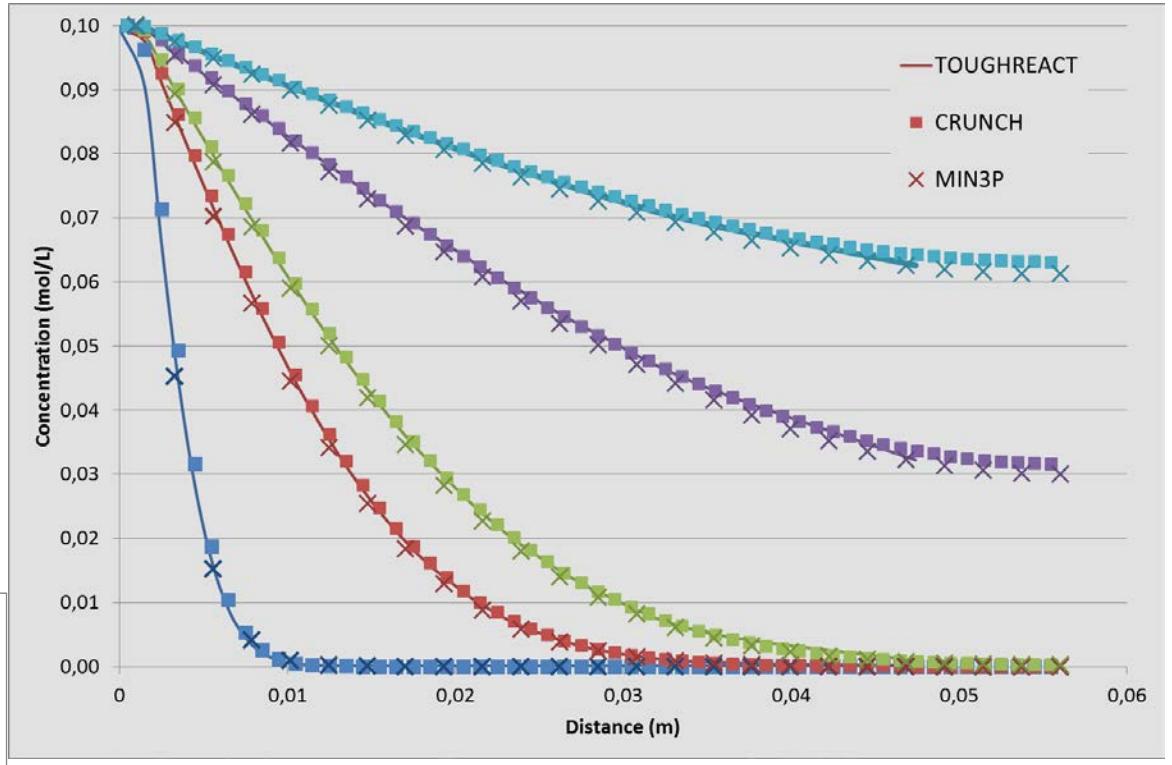
**→ OK to use Richards' equation for benchmarking exercise**

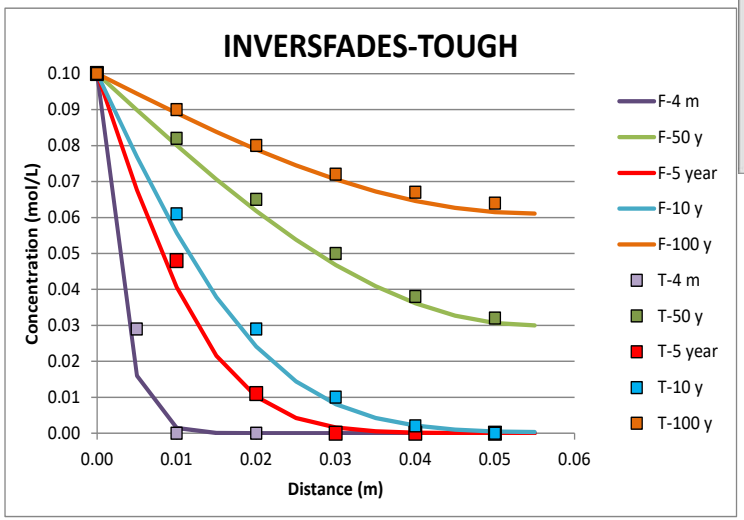
# COMPONENT 2: REACTION TRANSPORT RESULTS AT CONSTANT $S_L$

## Making sure the same effective diffusion coefficient is used…

**coupling equation** (Millington-Quirk relationship):

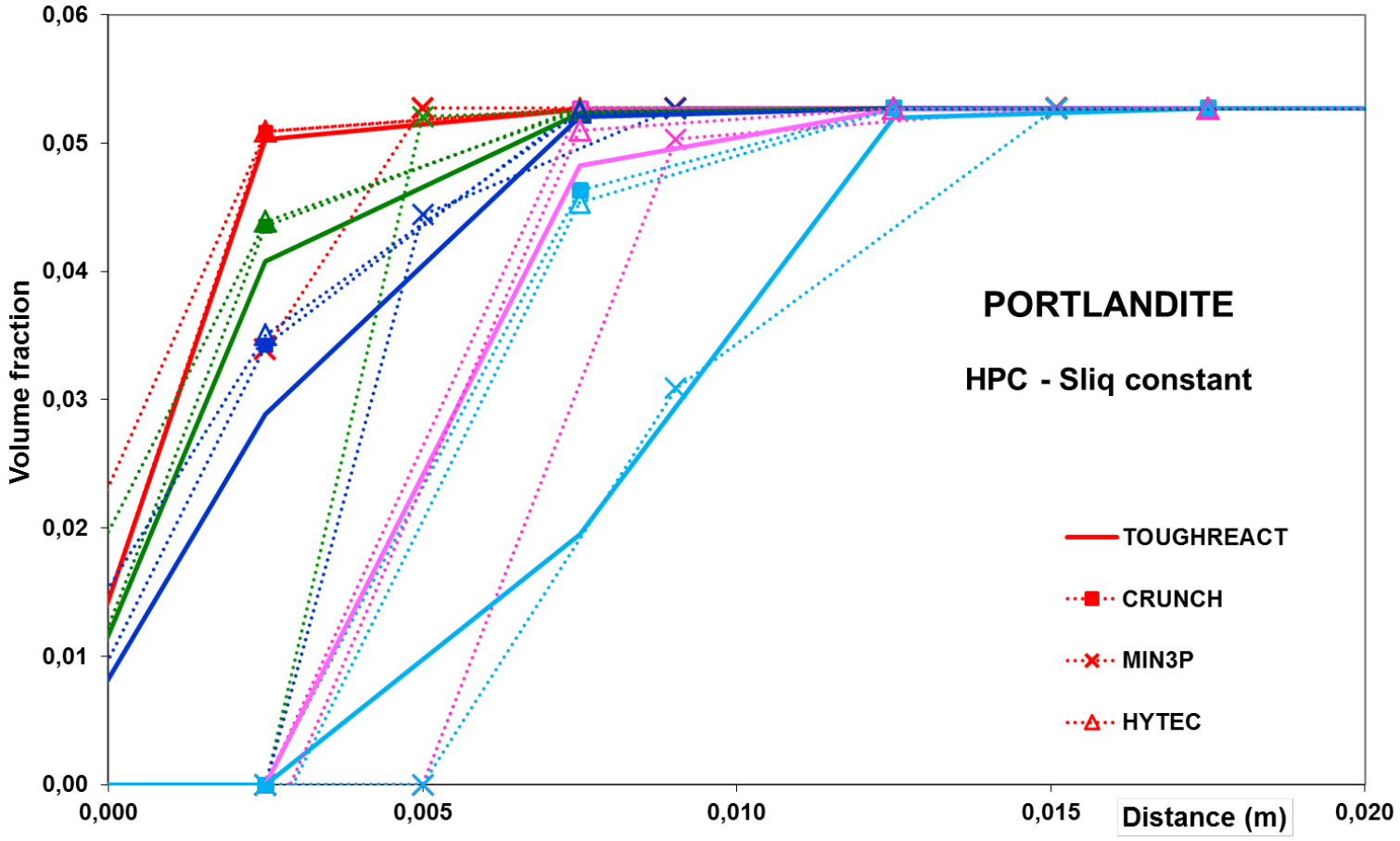
$$D_{eff} = D_0 \omega^a S_l^b$$



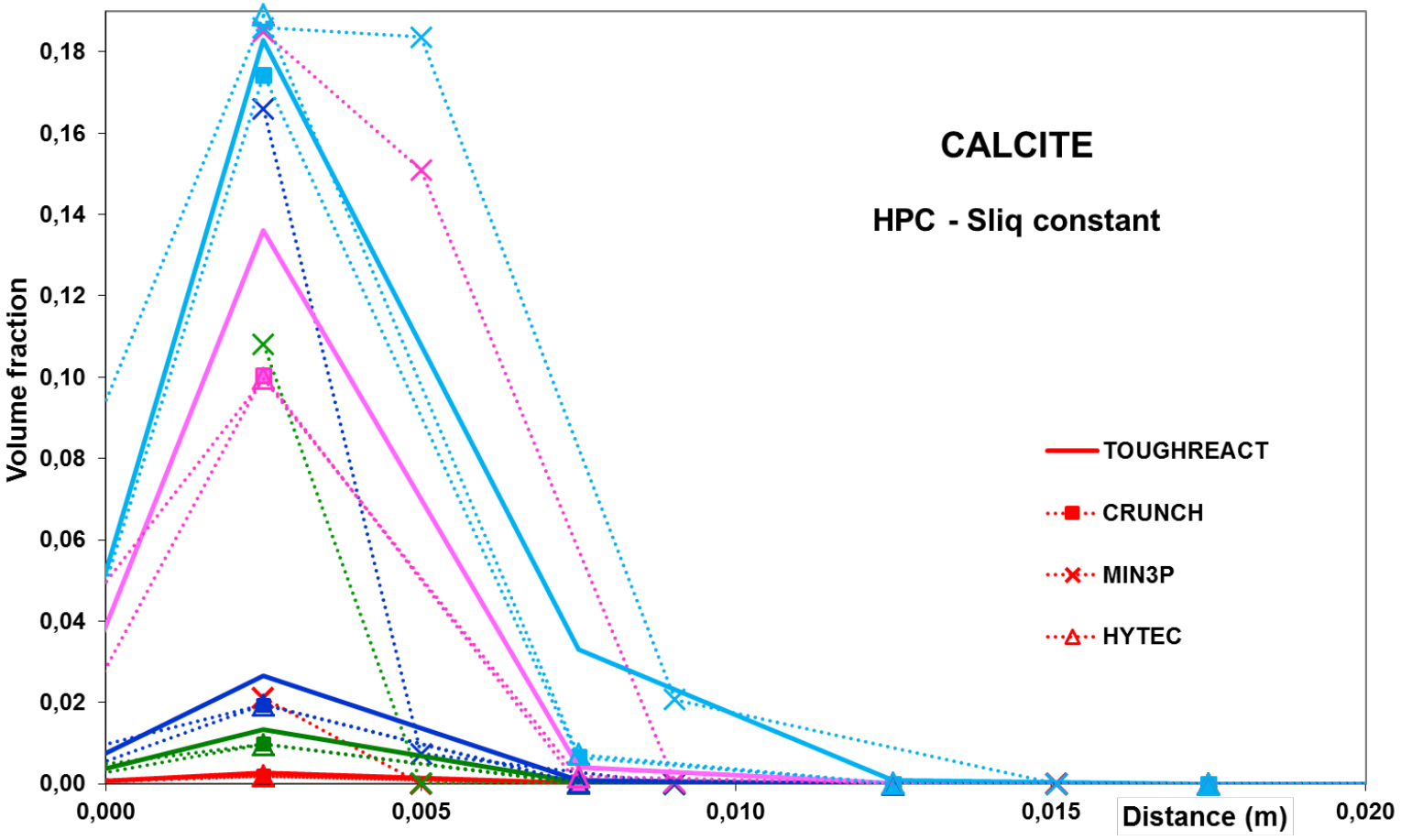

For Crunchflow, b = 3.2 has to be used (instead of b = 4.2 for Toughreact)

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



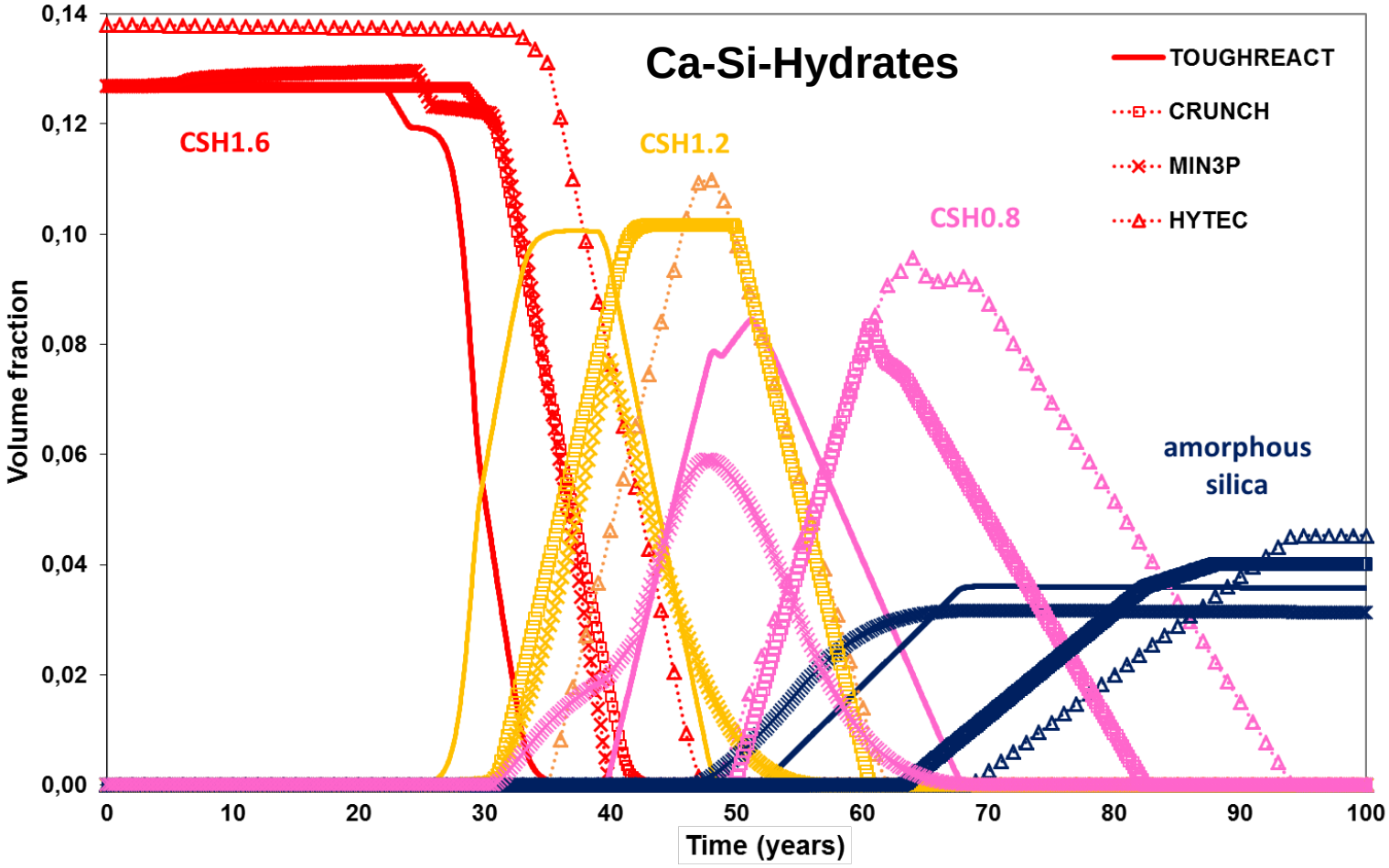

**Carbonation front is similar, but the size of grid cells limits precise comparison**

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



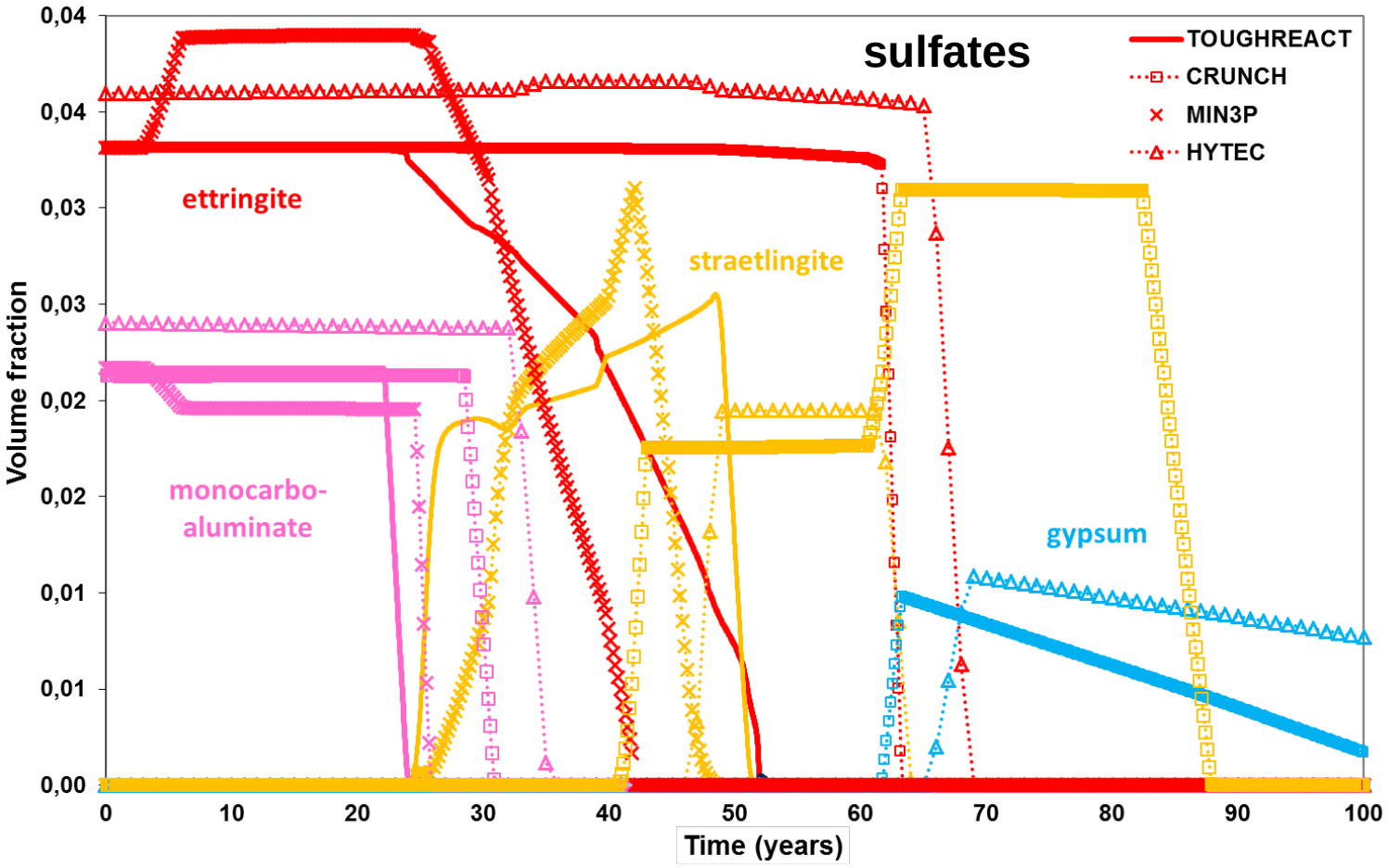

**Calcite precipitation front is similar (MIN3P a little ahead of time/distance)**

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



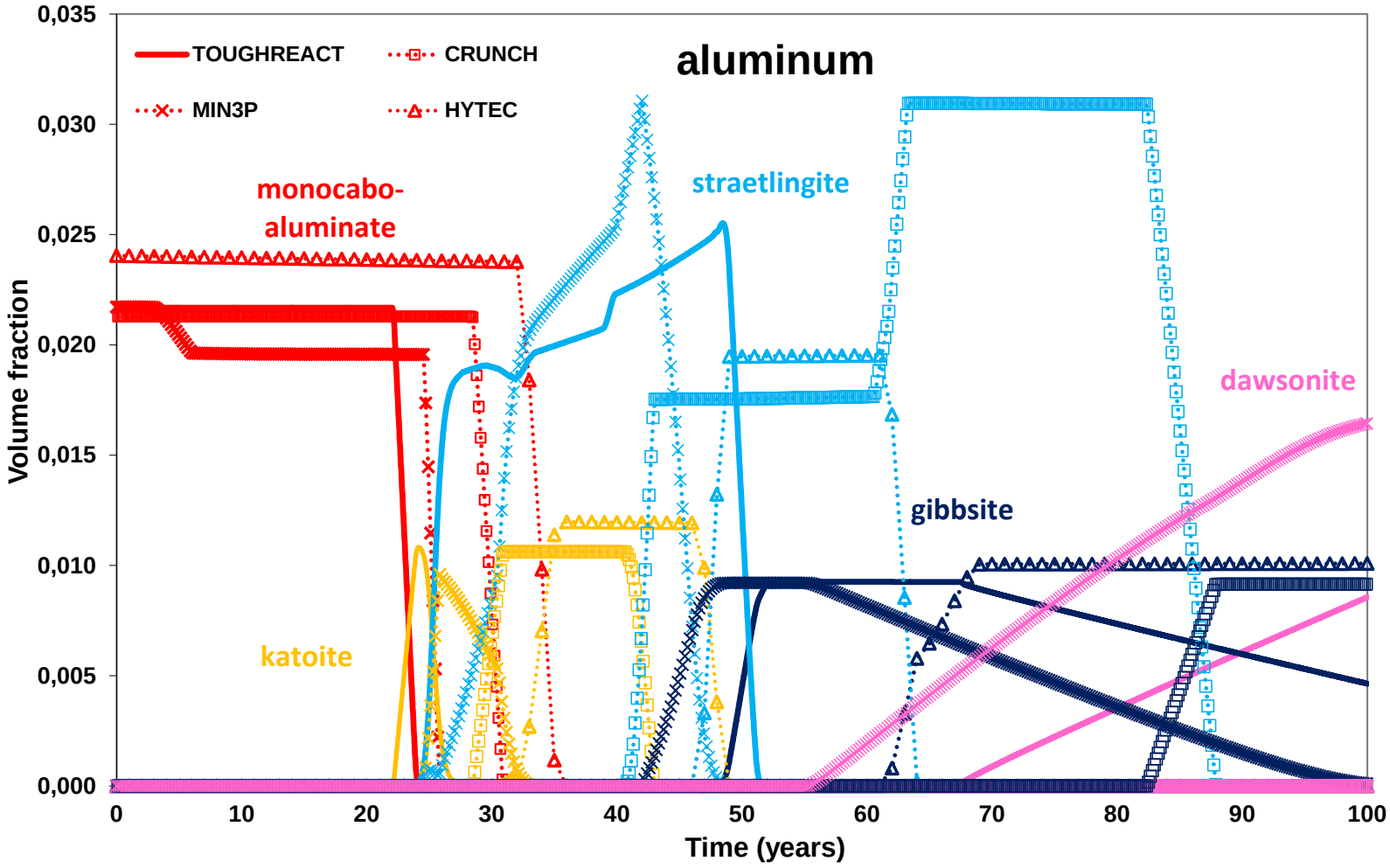

**Same mineral paragenesis but timing not exactly the same for all codes**

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



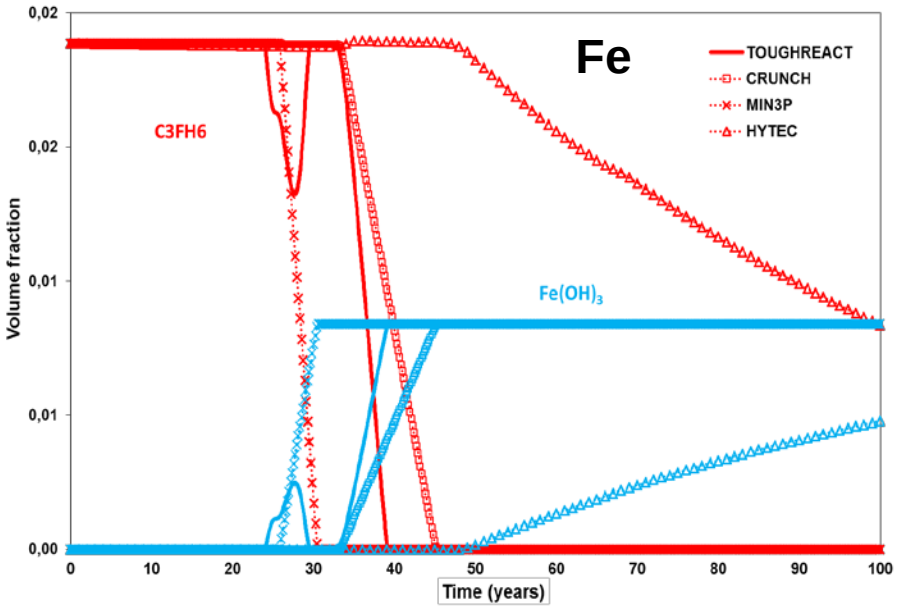

**Precipitation of gypsum in the simulation with Crunchflow and Hytec**

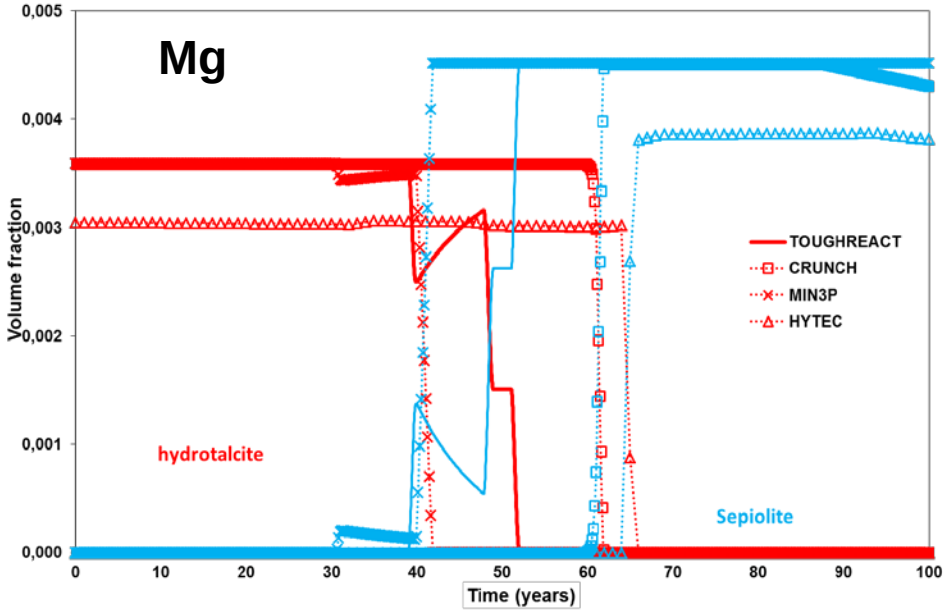
# COMPONENT 2B: CONCRETE CARBONATION AT CONSTANT $S_L$




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

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



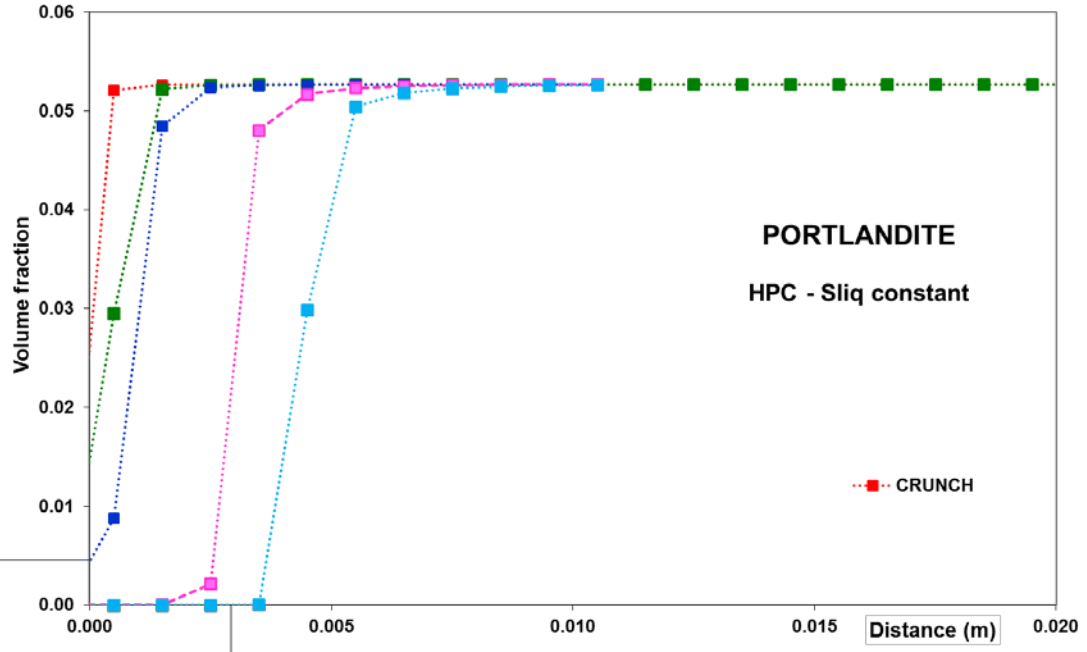



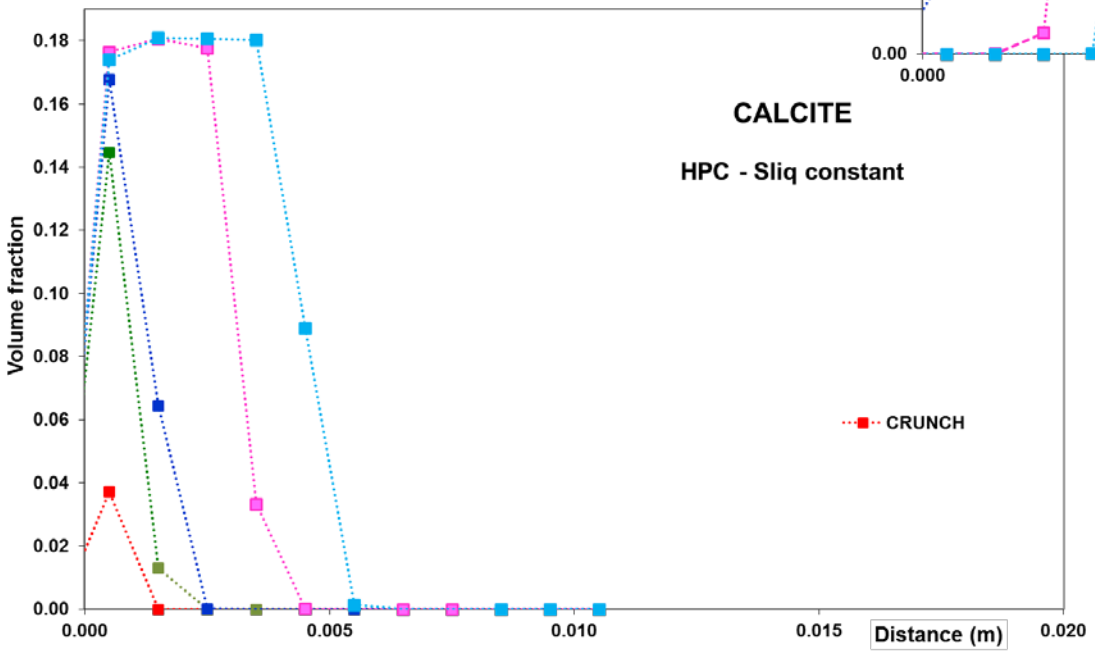

**Same mineral paragenesis but timing not exactly the same for all codes**

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

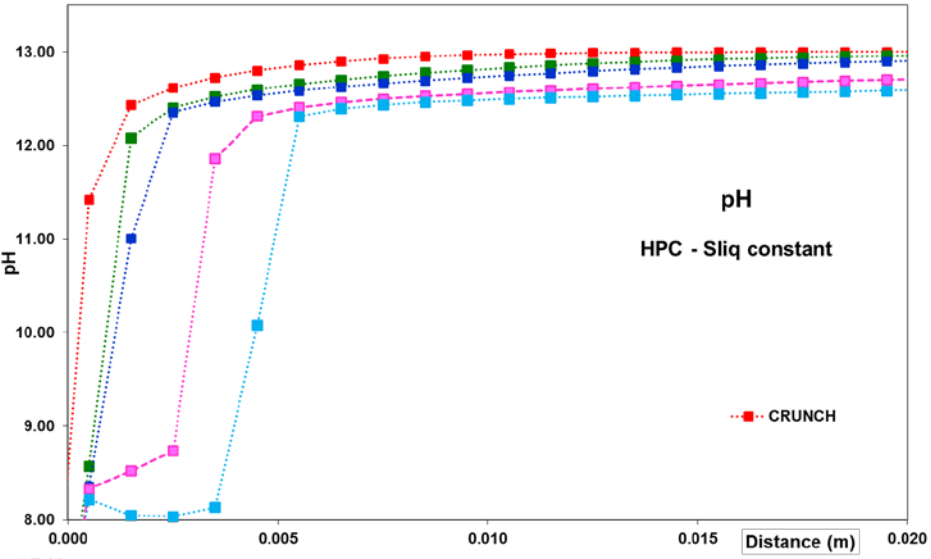
**The discrepancies observed in the complex prompted a simpler simulation case (component 2A) with only**

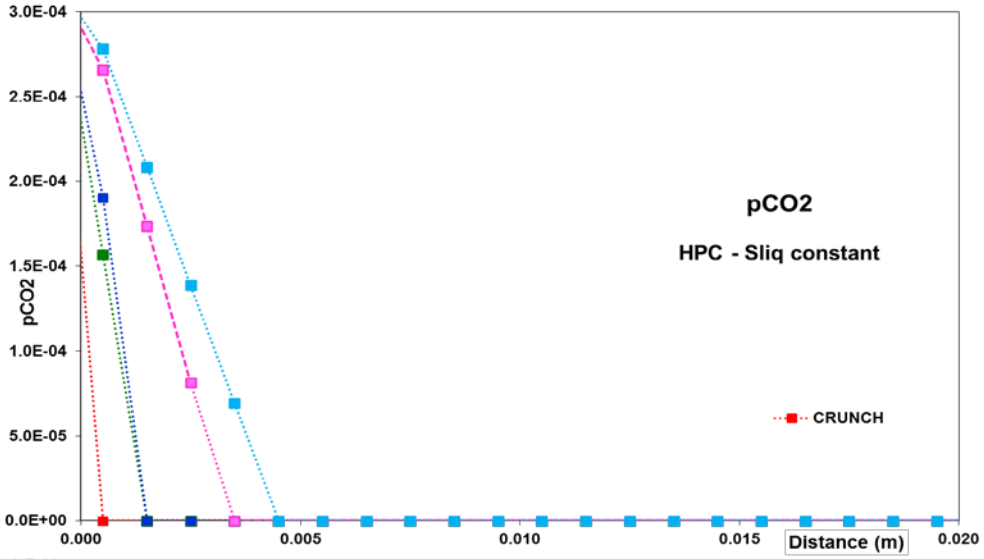
**Portlandite and Calcite**

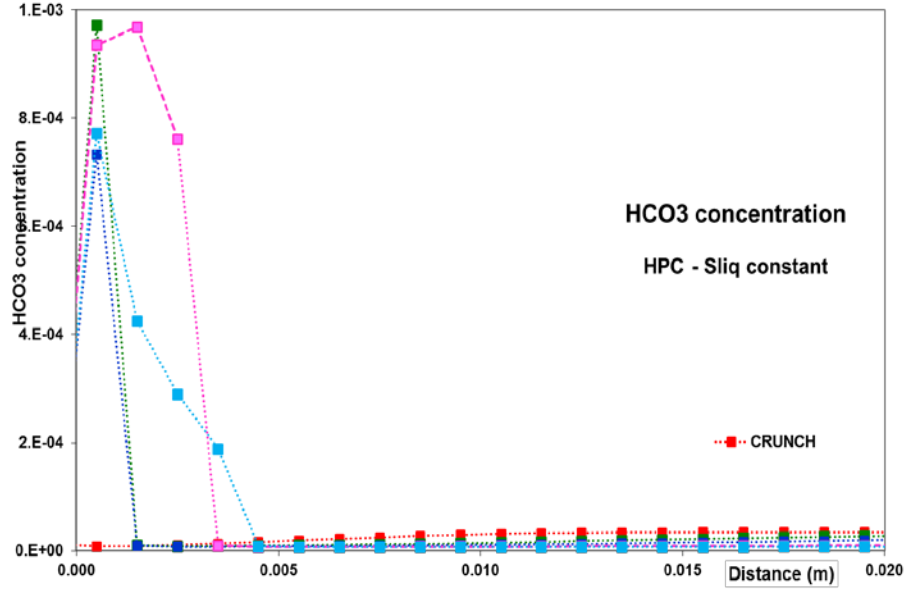


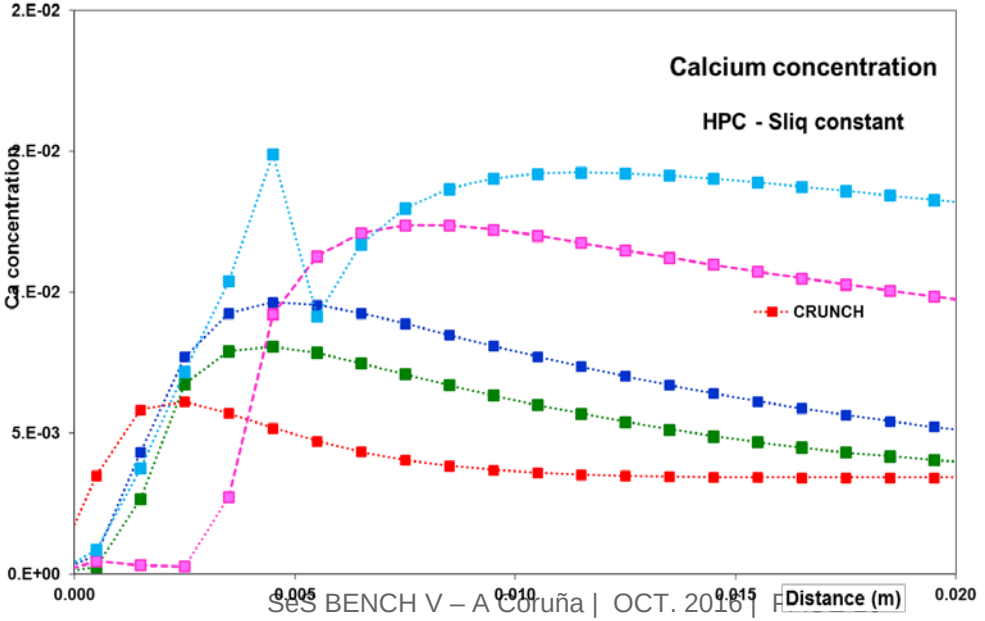



# COMPONENT 2A: PORTLANDITE-CALCITE SYSTEM AT CONSTANT $S_L$



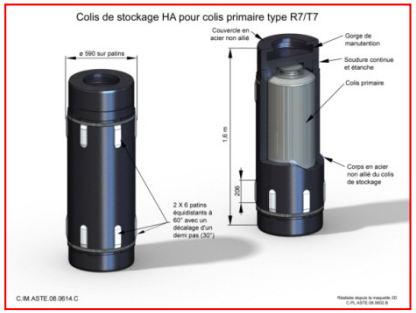



# CONCRETE CARBONATION SUMMARY

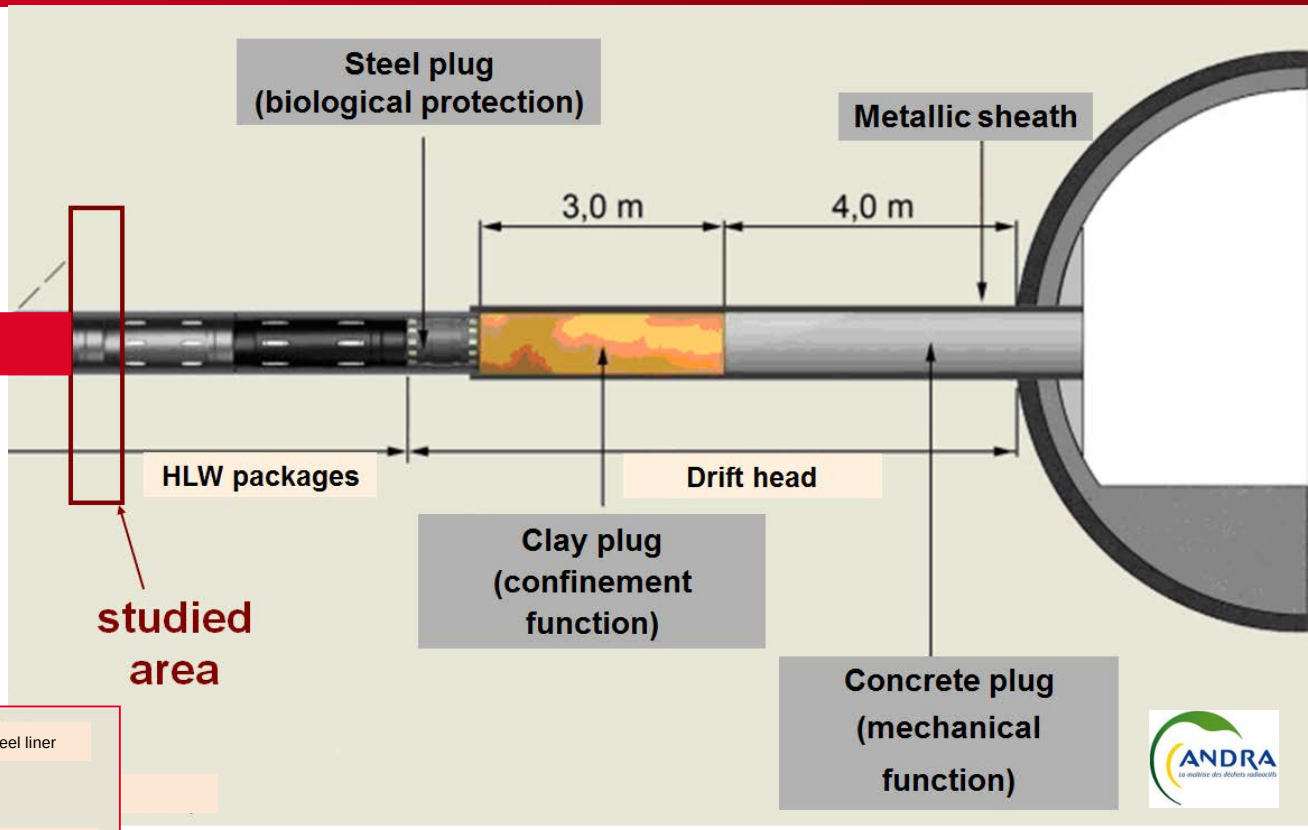
- ✓ Concrete carbonation exercise
  - ✓ differences between codes do not seem to be linked to the grid size or coupling method
  - ✓ differences in results attributable to transport in the gas phase?
  - ✓ CPU concerns: no SIA → small time steps → CPU times go up !
- ✓ Component 2a with simplified chemistry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

# Glass & steel corrosion and redox control in claystones

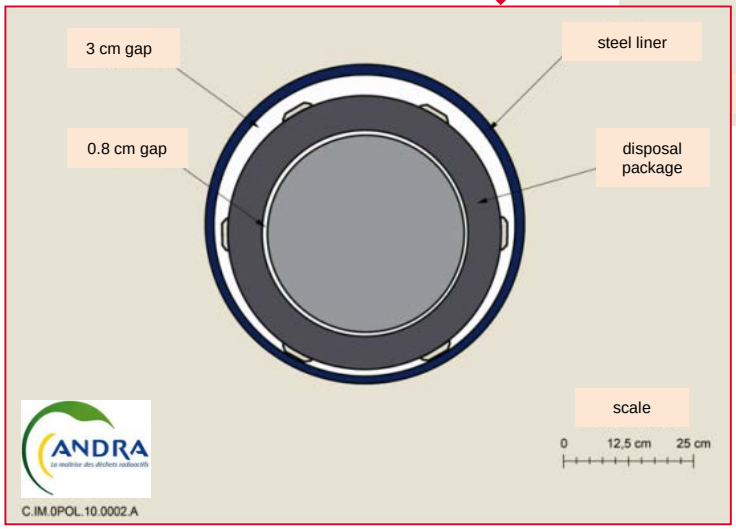
# HLW DISPOSAL CELL




Vitrified waste packages




Cross section



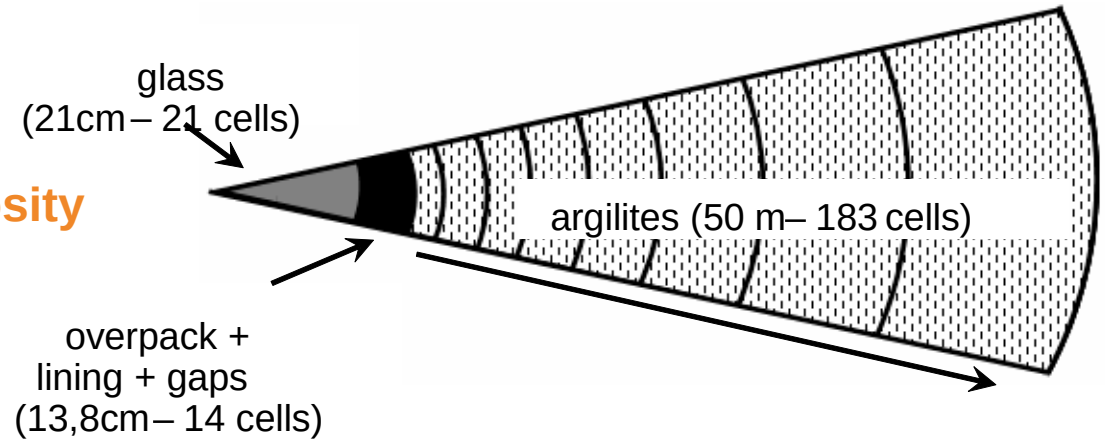

- different types of material in physical contact, technological gaps

→ **long term calculations of geochemical evolution (100 000 years)**

# GEOMETRY AND TRANSPORT PROPERTIES

- **1D radial domain**
- **transport: diffusion only**
- **water saturated, constant porosity**
- **isothermal conditions**
- **$H_2$(g) from anoxic corrosion**

  **$pH_{2(max)}$ = 60 bar**




- glass

  Φ = 0.42 m, H = 1 m

  porosity = 0.12

- metallic components

  total thickness = 0,095 m,

  porosity = 0.25

- connected fractured zone

  0.4 * excavation diameter = 0.268 m

  porosity = 0.20; $D_{eff}(25°C) = 5.2\ 10^{-11}\ m^2/s$

- undisturbed claystone (50 m)

  porosity = 0.18; $D_{eff}(25°C) = 2,6\ 10^{-11}\ m^2/s$

**Major challenge comes from:**

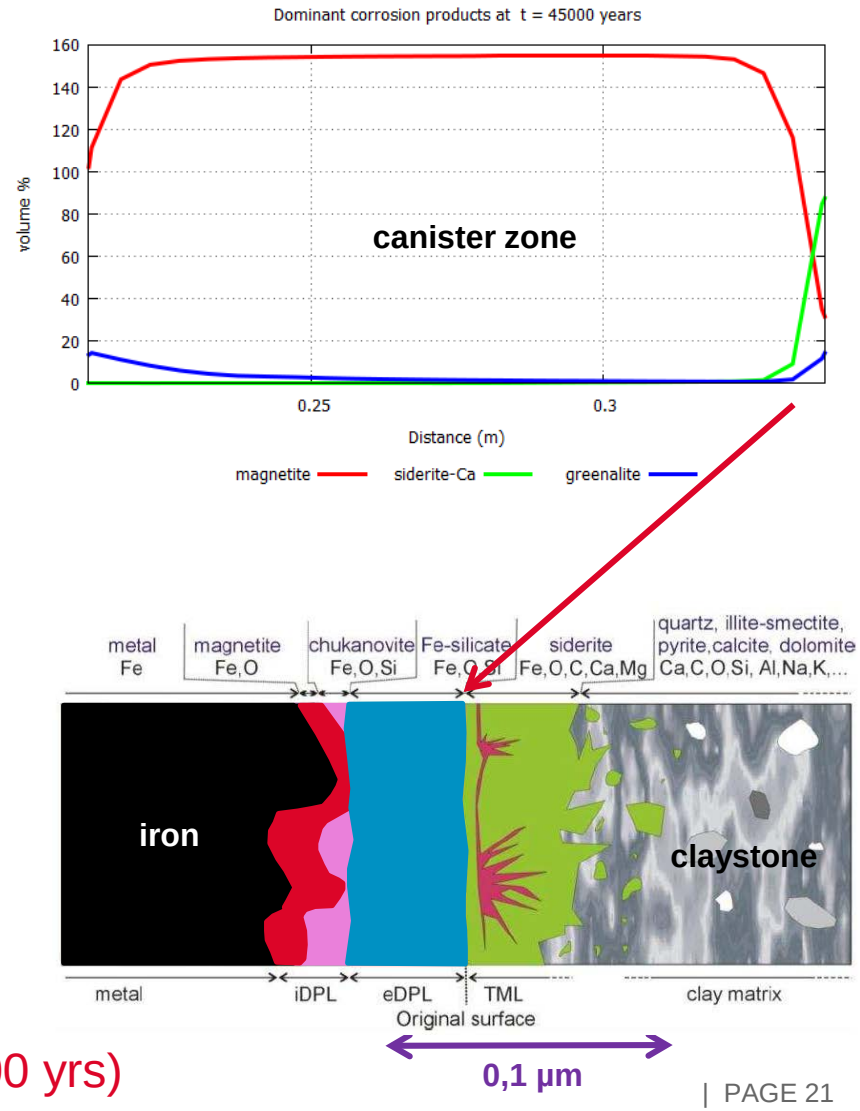
- **highly reactive system (strong pH and redox perturbation)**
- **complex geochemical system (15 chemical elements, 80 aqueous species, 60 minerals)**

# EXISTING BENCHMARK SUB-COMPONENTS

## 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

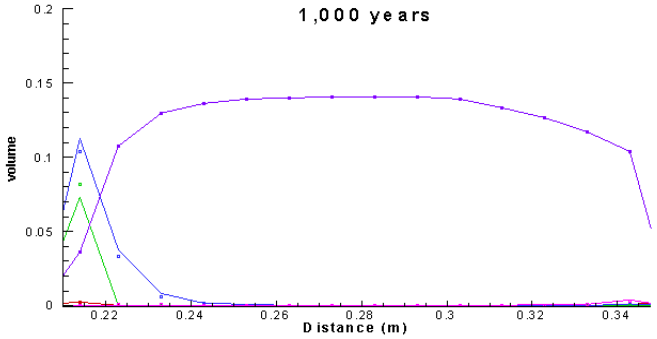
→ **more phenomenological model for corrosion**

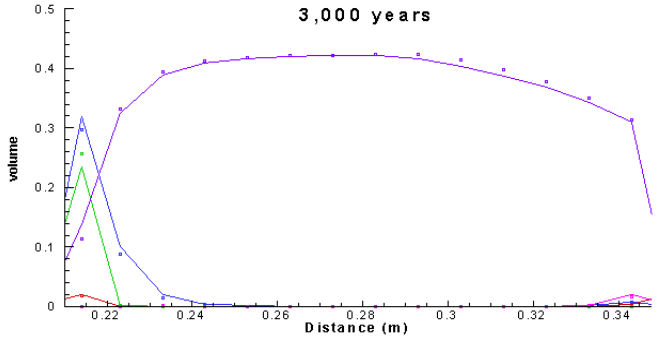



## Component 2: iron corrosion + glass alteration (100 000 yrs)

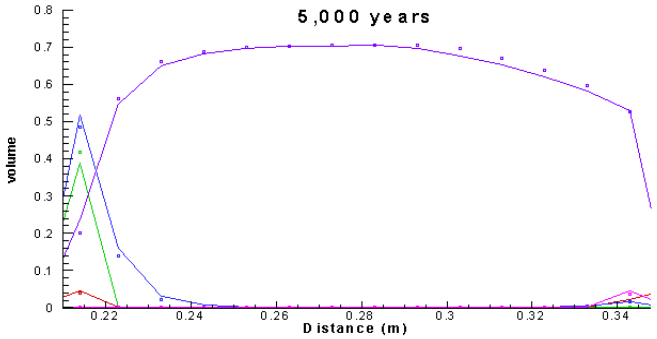
# COMPONENT 1: RESULTS IN THE BASE CASE

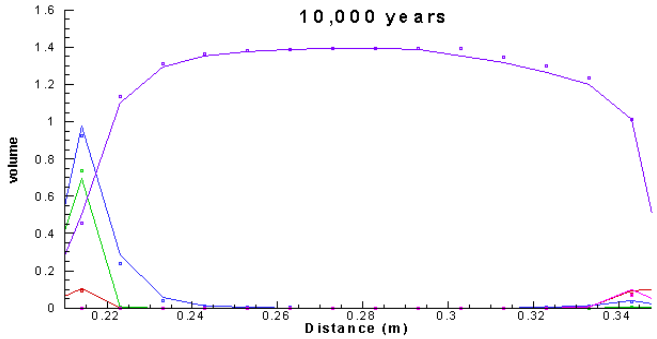
ONLY 2 CODES : MIN3P-Crunchflow (a very good agreement is obtained!) …

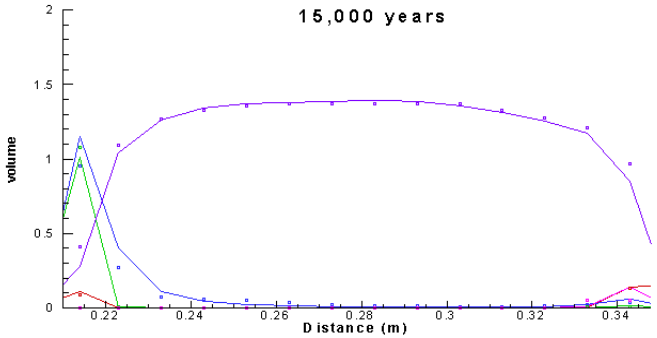


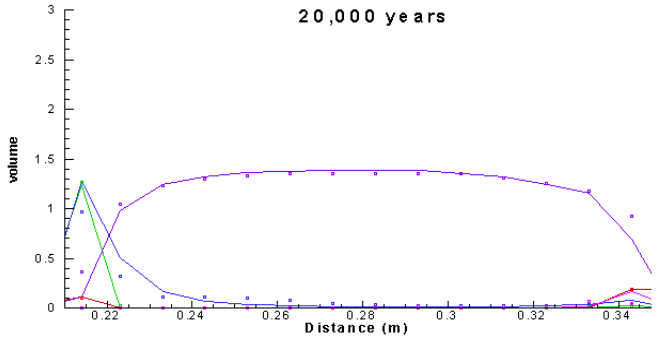




**in the iron zone**



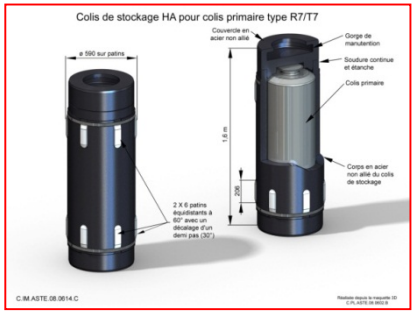



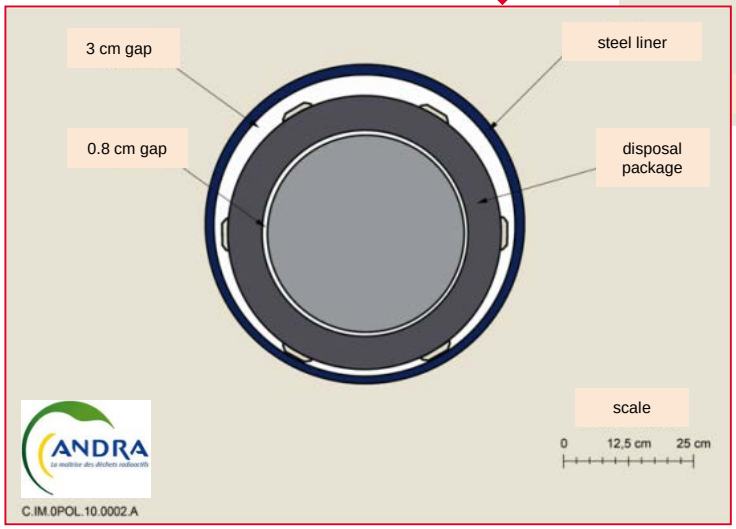


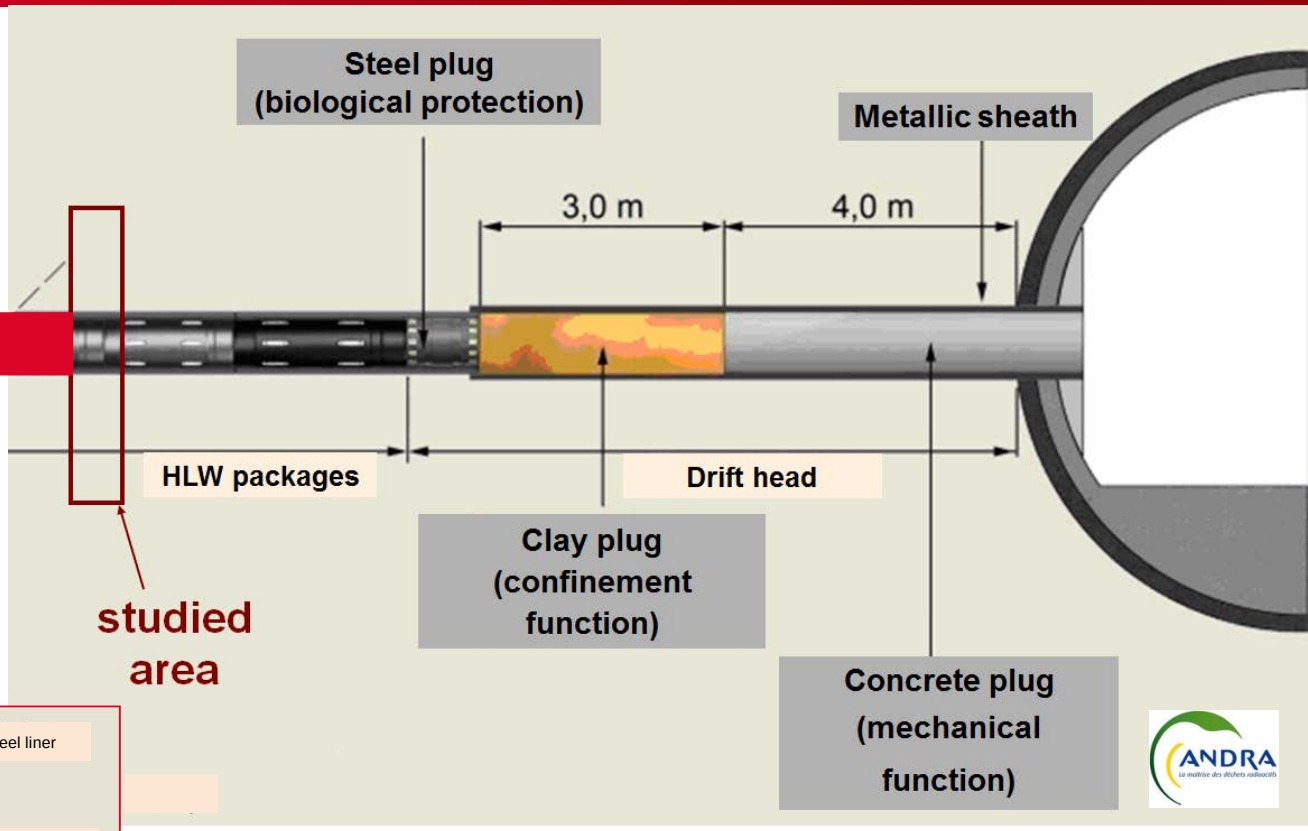

# CORROSION IN HLW DISPOSAL CELL




Vitrified waste packages

Cross section



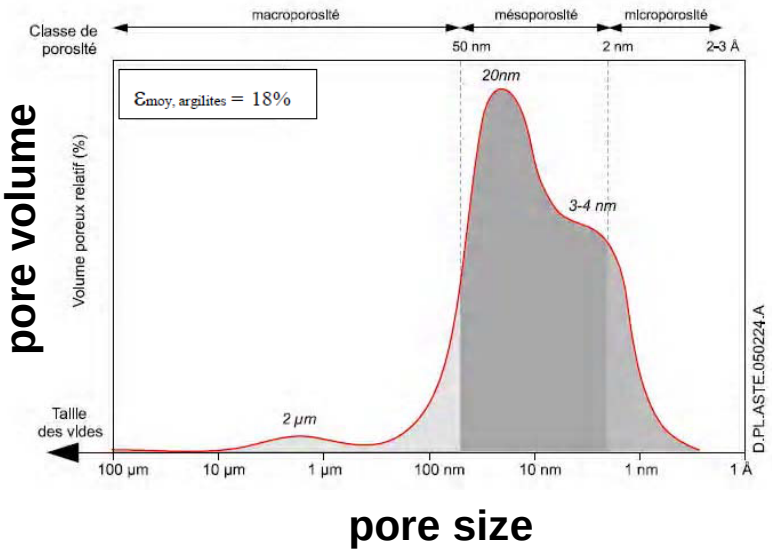



# RELATED TOPICS

- **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

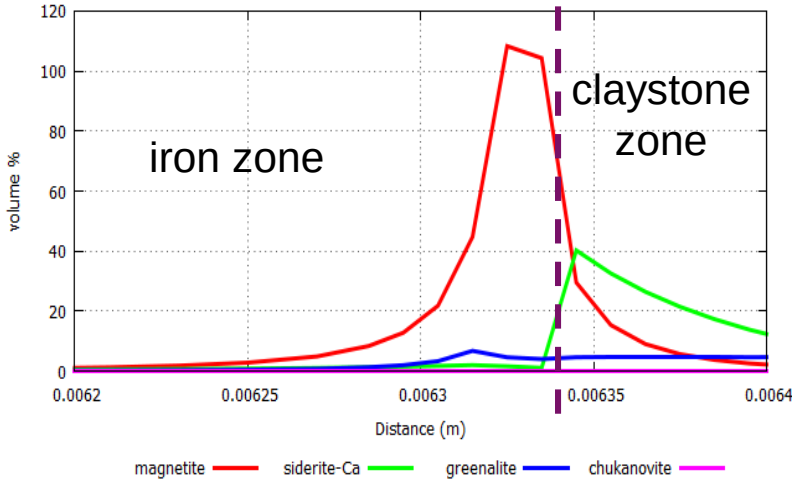
# STEEL CORROSION "GEOCHEMICAL" REACTION

## ✓ Corrosion in reactive transport codes

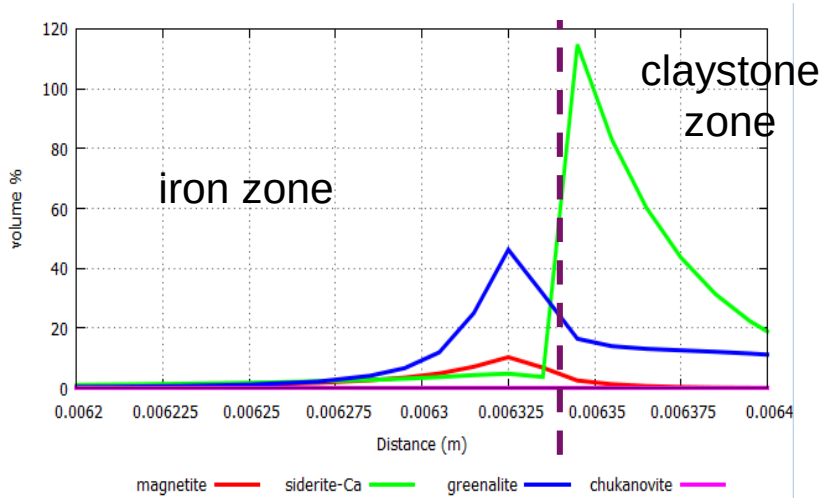
### ✓ changes in pH and Eh occur through:

$$Fe(s) + 2\ H_2O \rightarrow Fe^{2+} + H_2 + 2\ OH^-$$

base case




corrosion rate /10

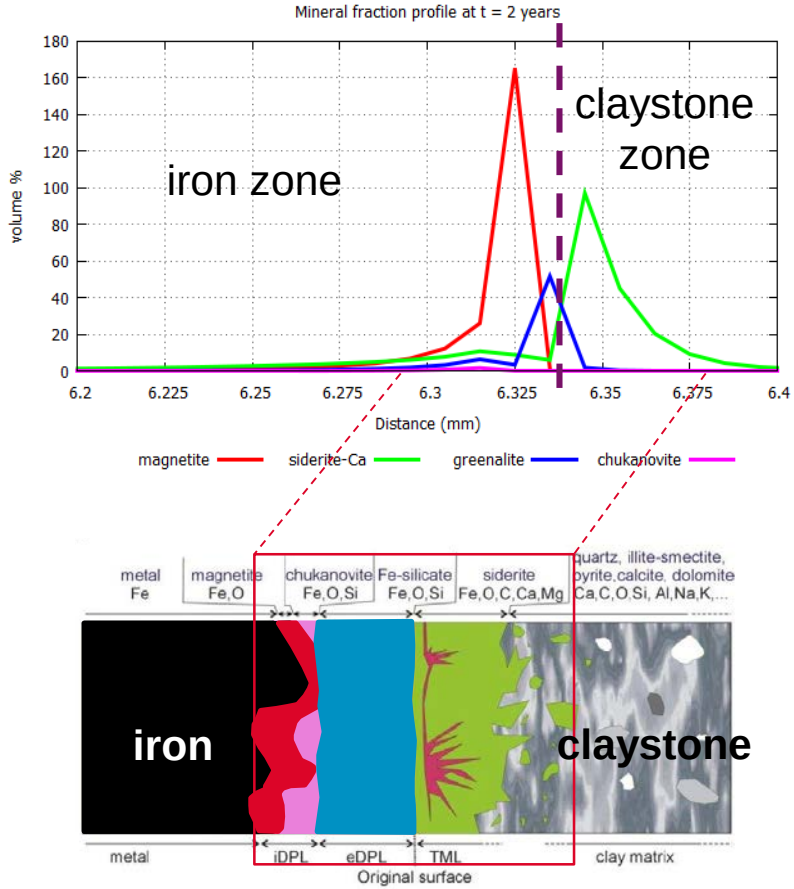


# STEEL CORROSION "GEOCHEMICAL" REACTION

… but the paragenesis of secondary minerals is not predicted correctly

To match the mineralogical paragenesis, we have to modify:

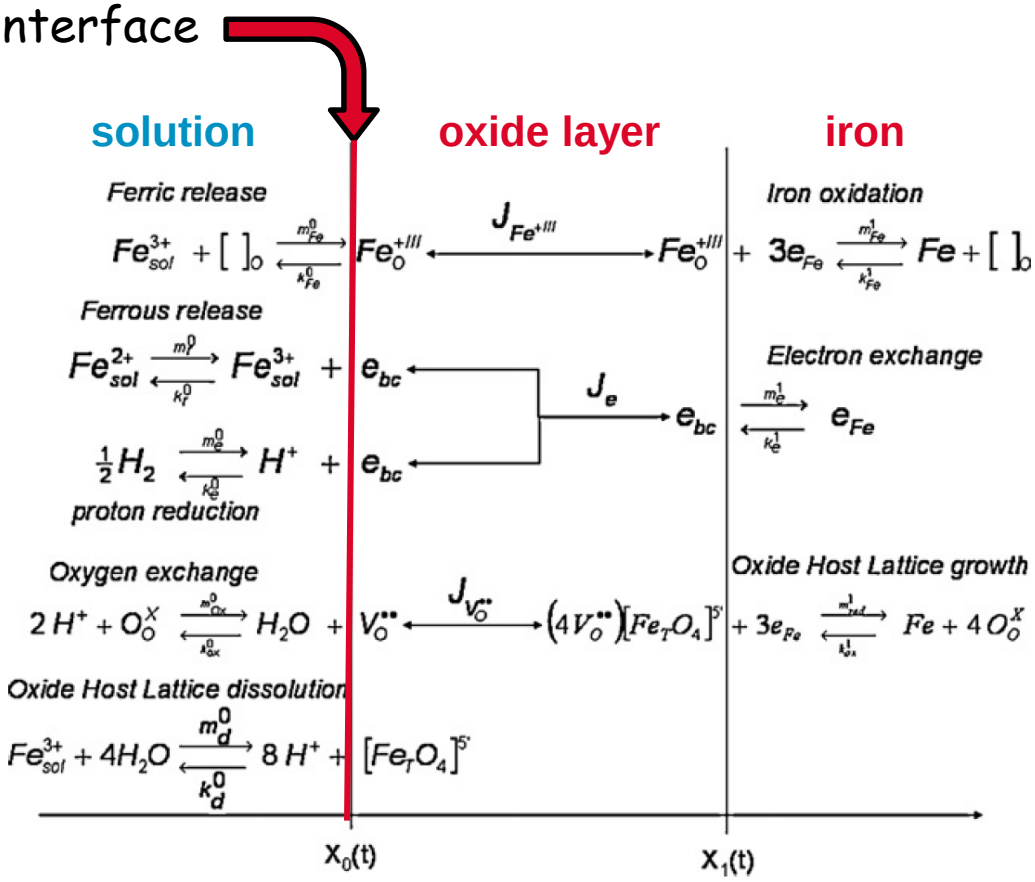
- (very low) diffusional properties in the corroded layer
- (high) magnetite precipitation rate




*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

# CONCLUSIONS

- ✓ Coupling of electrochemical corrosion reactions with reactive transport codes:
  - ✓ use elemental fluxes (Fe, $H_2$)?
  - ✓ use mineral reaction rates (corrosion and oxide layer precipitation/dissolution)?
  - ✓ use fluxes for $Fe^{2+}$ and $Fe^{3+}$ and aqueous kinetics?

# THANK YOU FOR YOUR ATTENTION

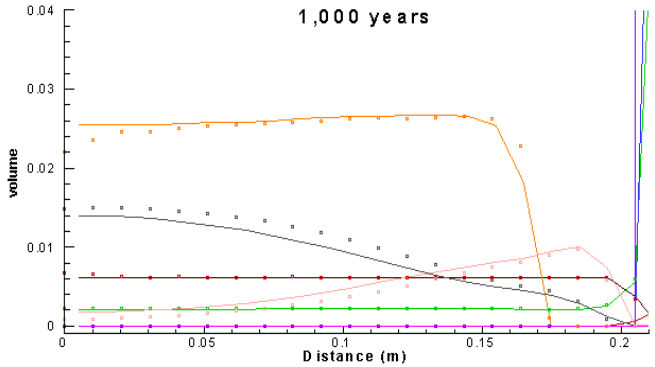
Commissariat à l'énergie atomique et aux énergies alternatives
Centre de Cadarache | 13108 Saint Paul-lez-Durance
T. +33 (0)4 42 25 37 24 | F. +33 (0)4 42 25 62 72

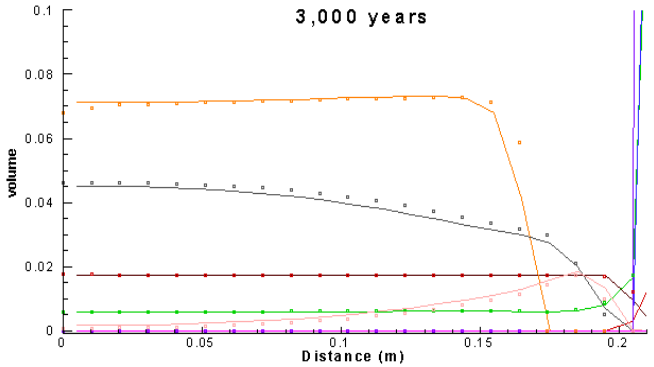
Etablissement public à caractère industriel et commercial | RCS Paris B 775 685 019

Direction de l'Energie Nucléaire
Département des Technologies Nucléaires
Service de Modélisation des Transferts et de Mesures Nucléaires

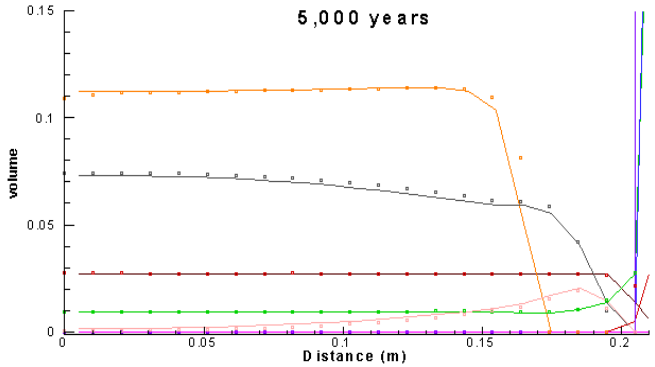
# Update on glass/iron/clay benchmark

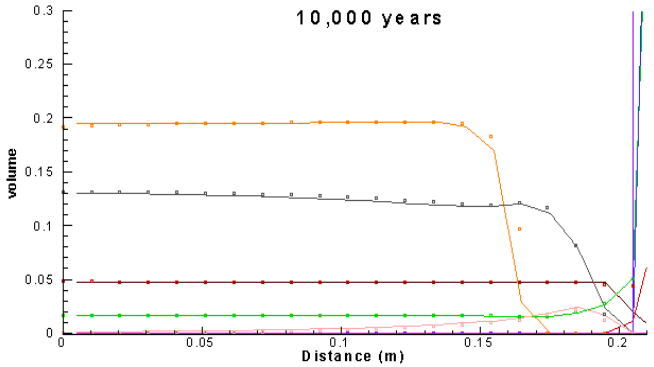
# RESULTS IN THE BASE CASE (3)

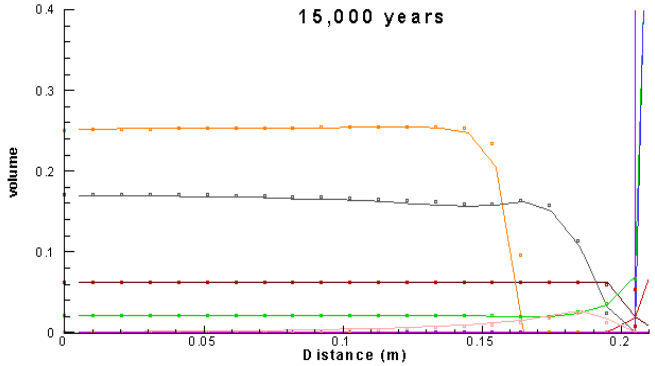


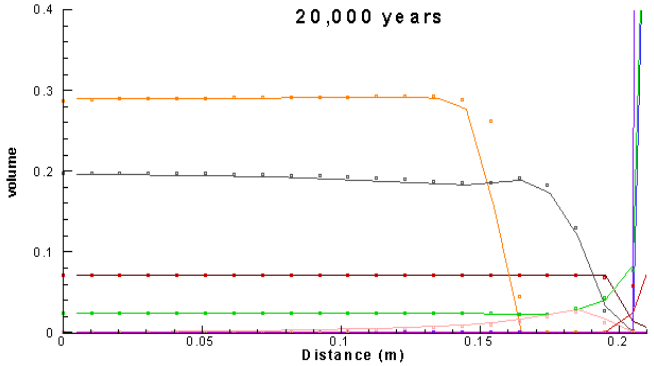



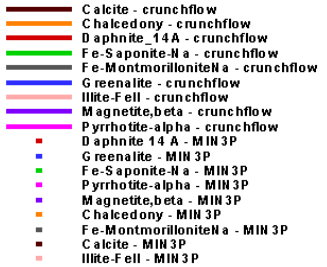

**in the glass zone**



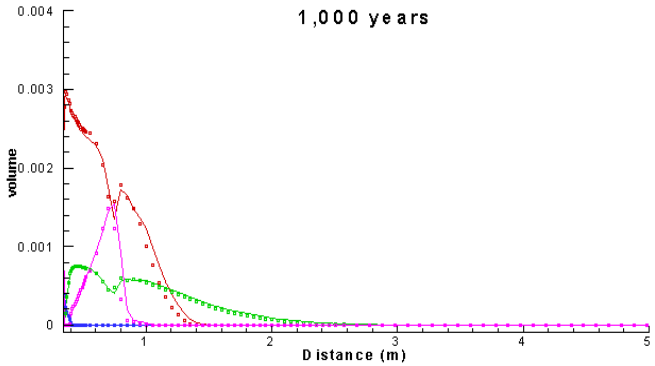



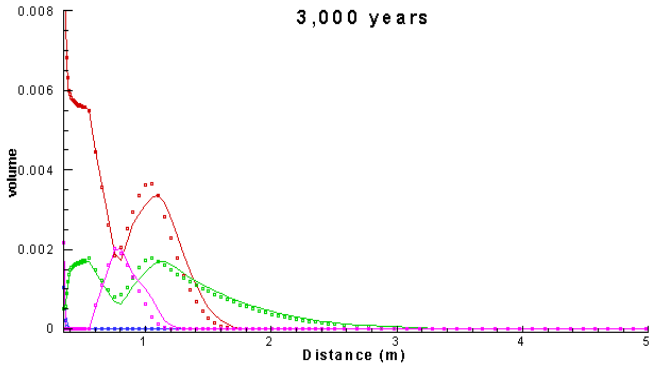



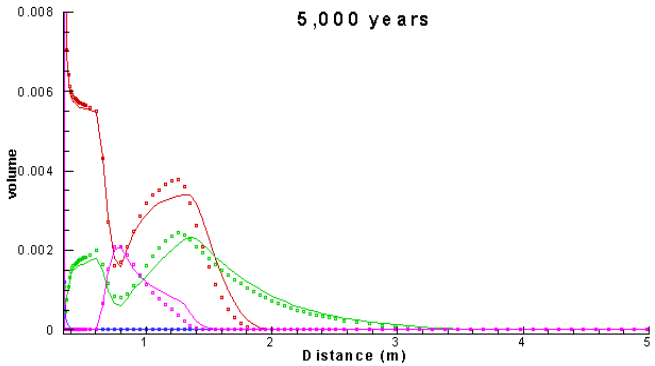



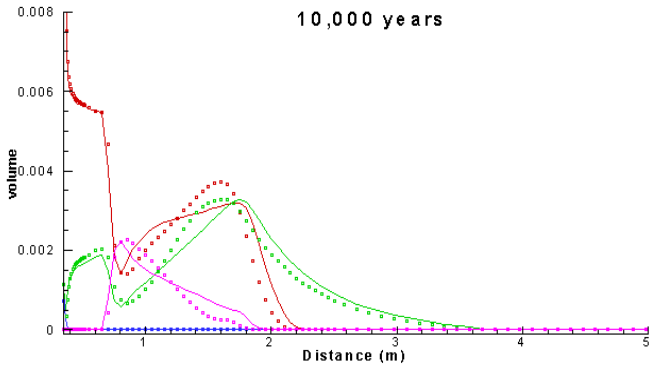



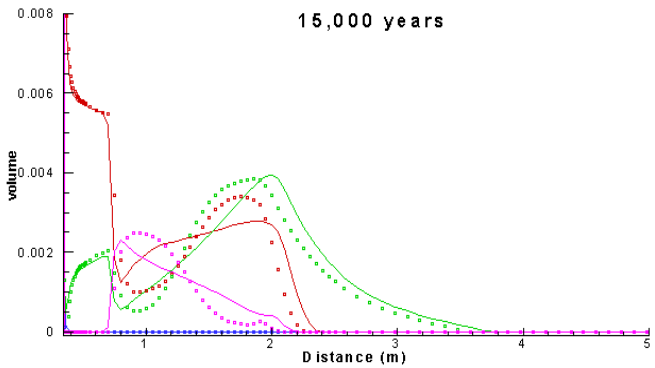
# RESULTS IN THE BASE CASE (4)

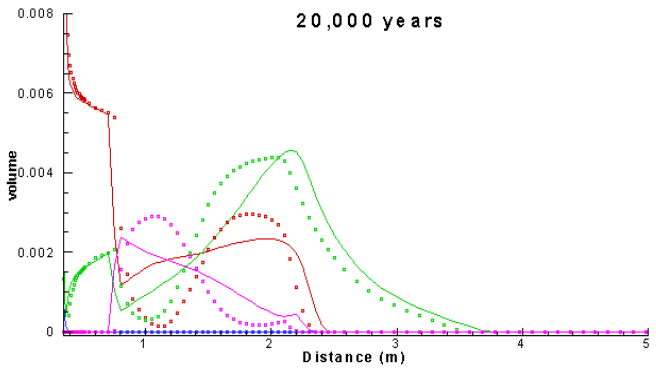



**in the clay zone**

