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

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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**

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CEA (French Alternative Energies and Atomic Energy Commission)

B. Cochepin, I. Munier

Andra (French Radioactive Waste Management Agency)

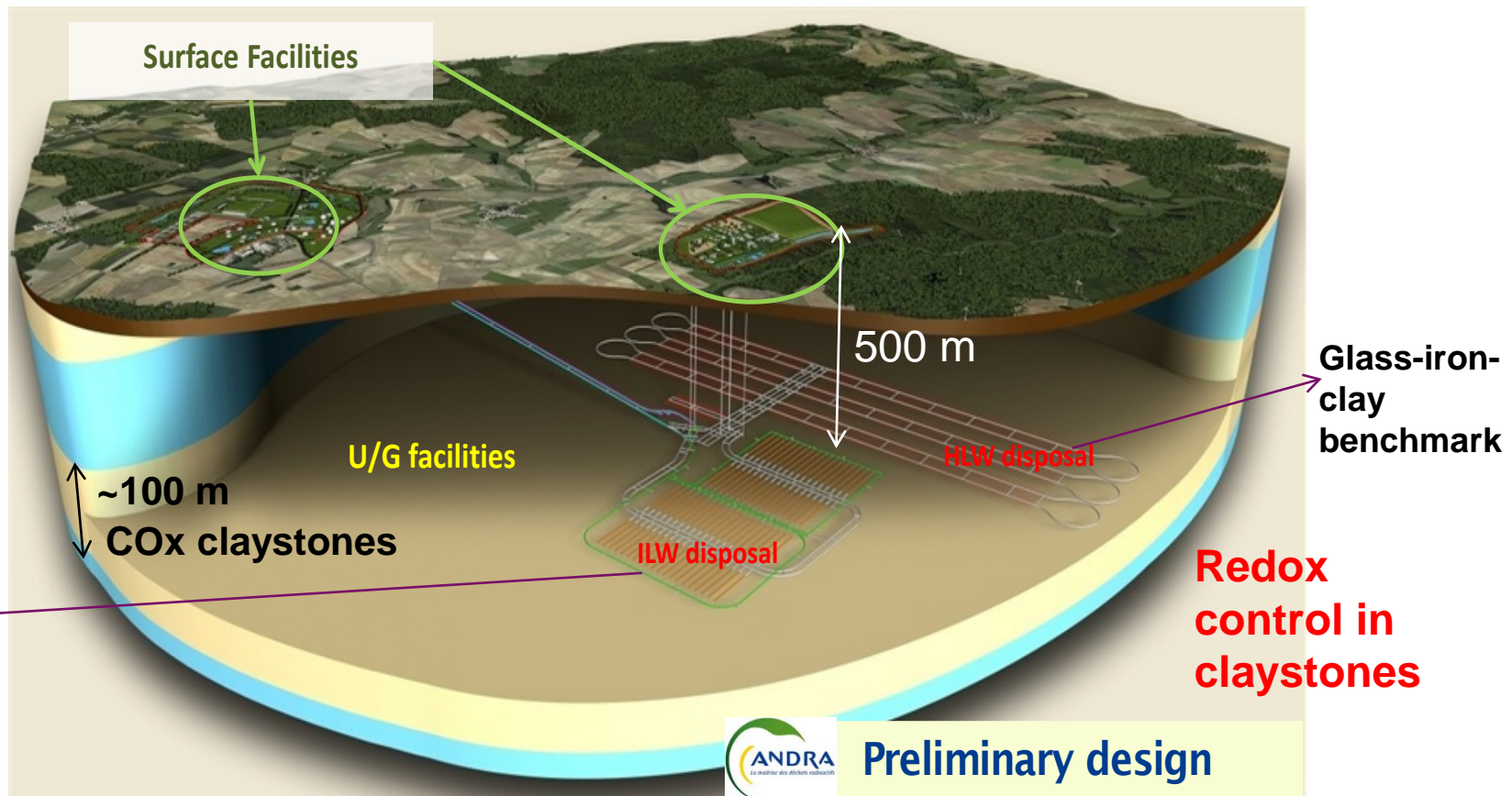


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SeS BENCH V – A CORUÑA - OCTOBER 13-15, 2016

DISPOSAL CONCEPT IN A CLAYSTONE FORMATION

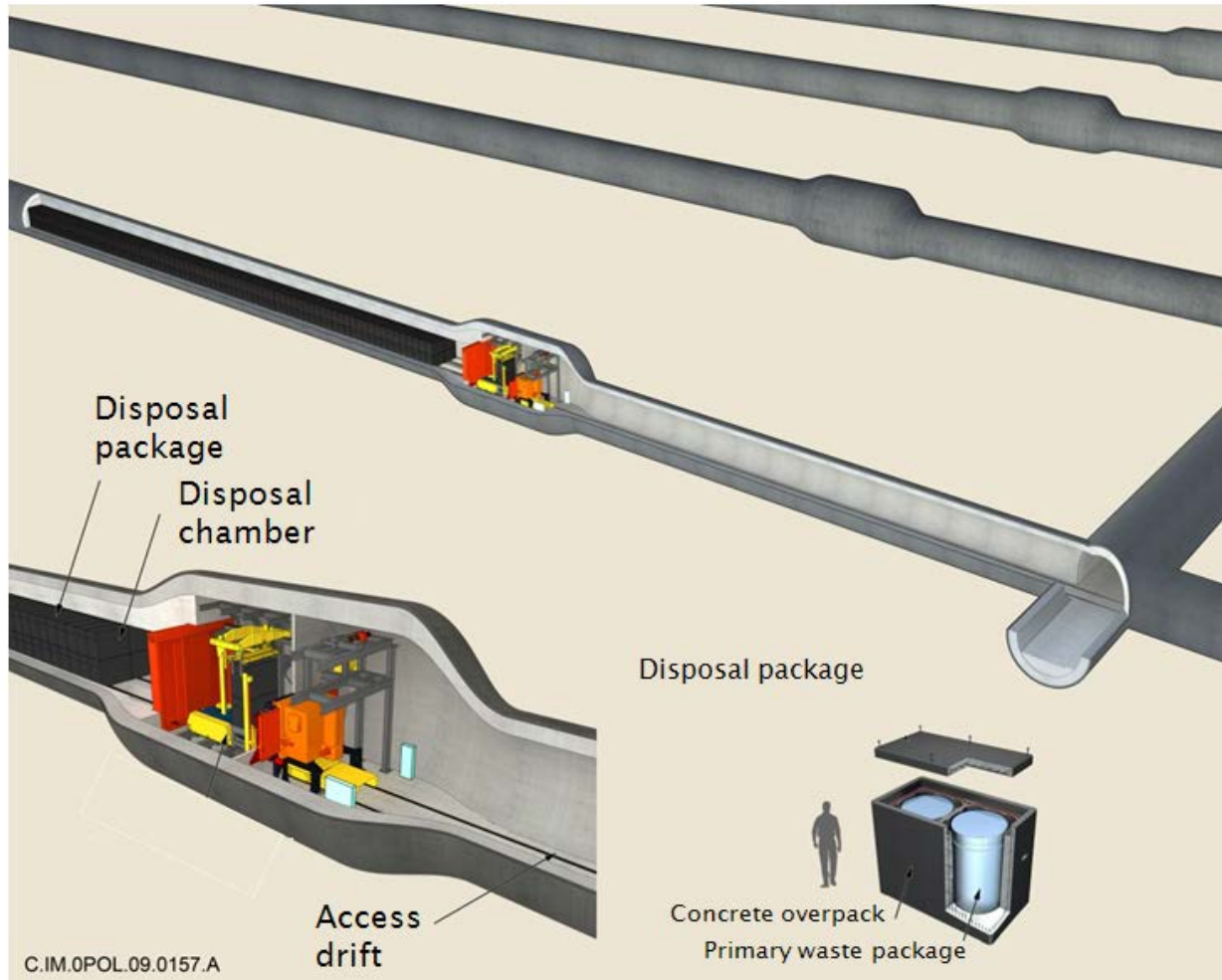
Current design of deep underground repository for high and intermediate level long-lived waste



**Update of the
atmospheric concrete
carbonation benchmark**

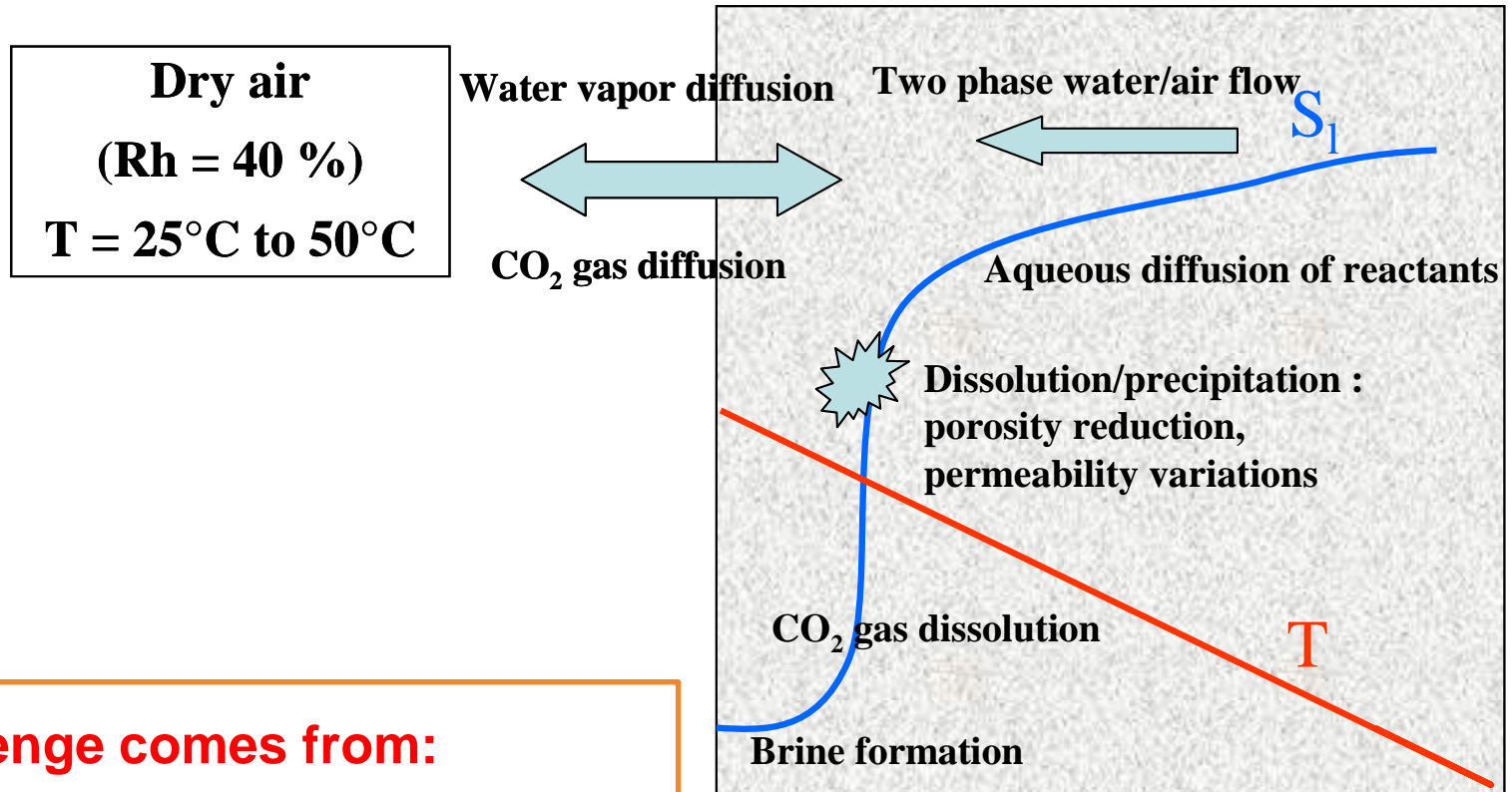
DESIGN: ILLW CELLS, SHAFTS (AND SEALS), ILLW DISPOSAL OVERPACK

Atmospheric carbonation of overpack during the operating period



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

DRYING AND CARBONATION PROCESSES OF ILLW OVERPACK

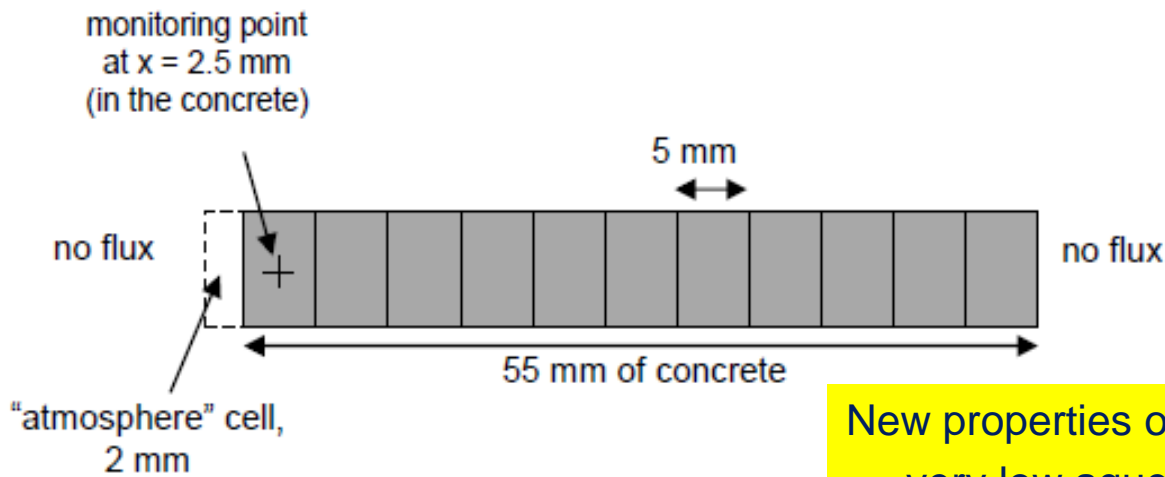


Major challenge comes from:

- CO₂ 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 ??

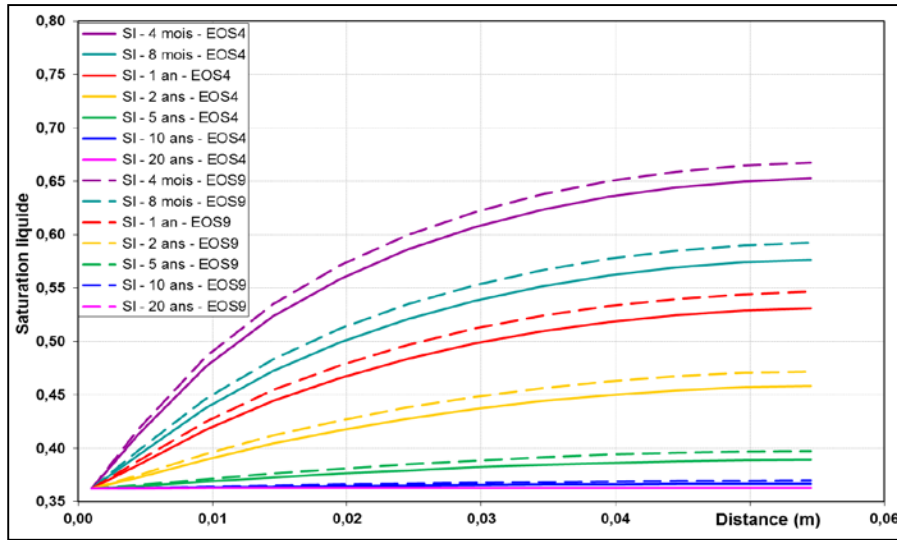
Drying with Richards' equation :

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

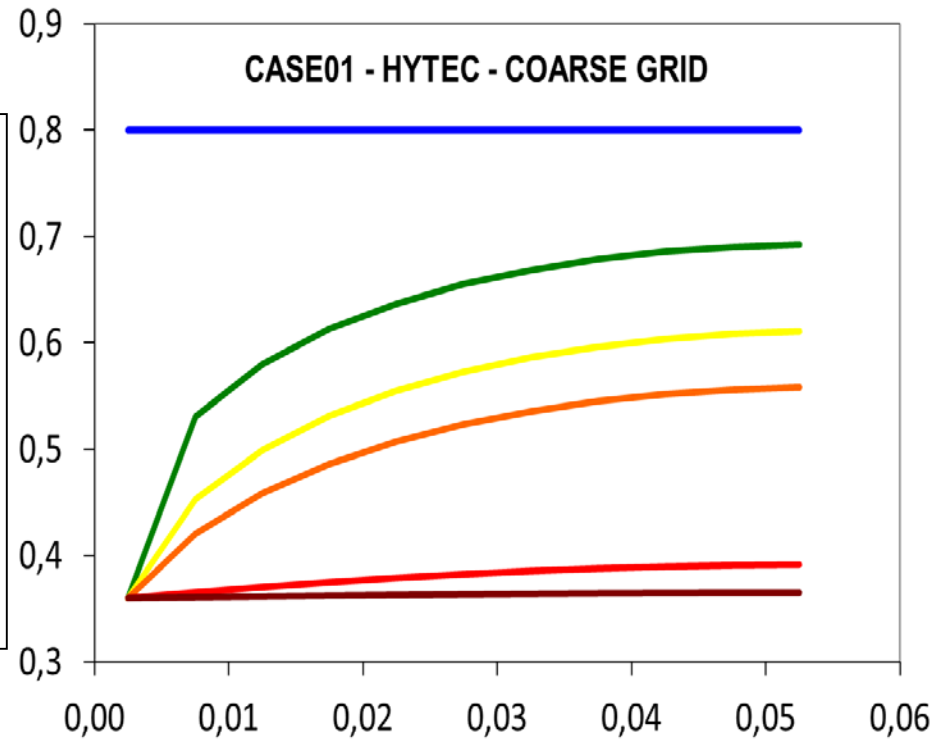
HYTEC (J. Corvisier, Mines Paristech)

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

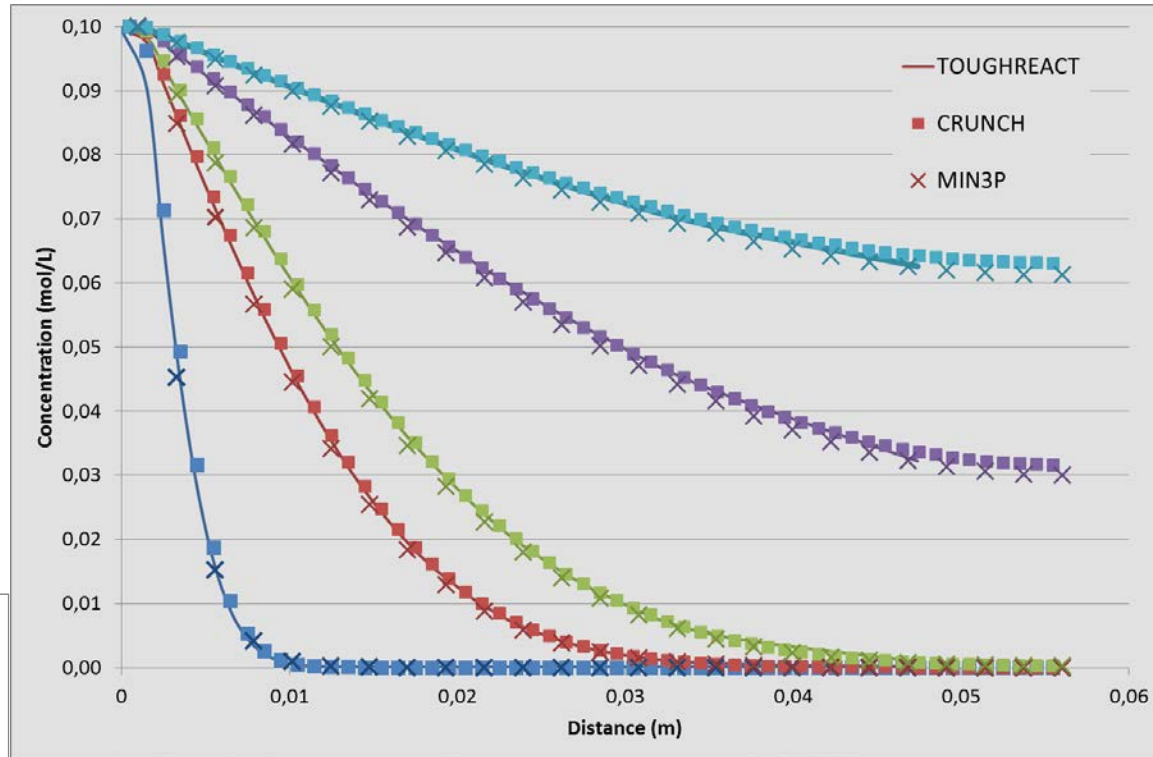
COMPONENT 2: REACTION TRANSPORT RESULTS AT CONSTANT S_L

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

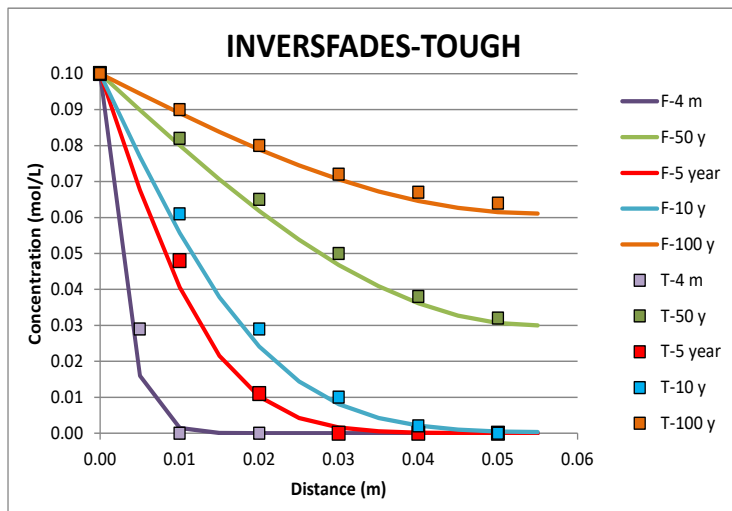
coupling equation

(Millington-Quirk relationship):

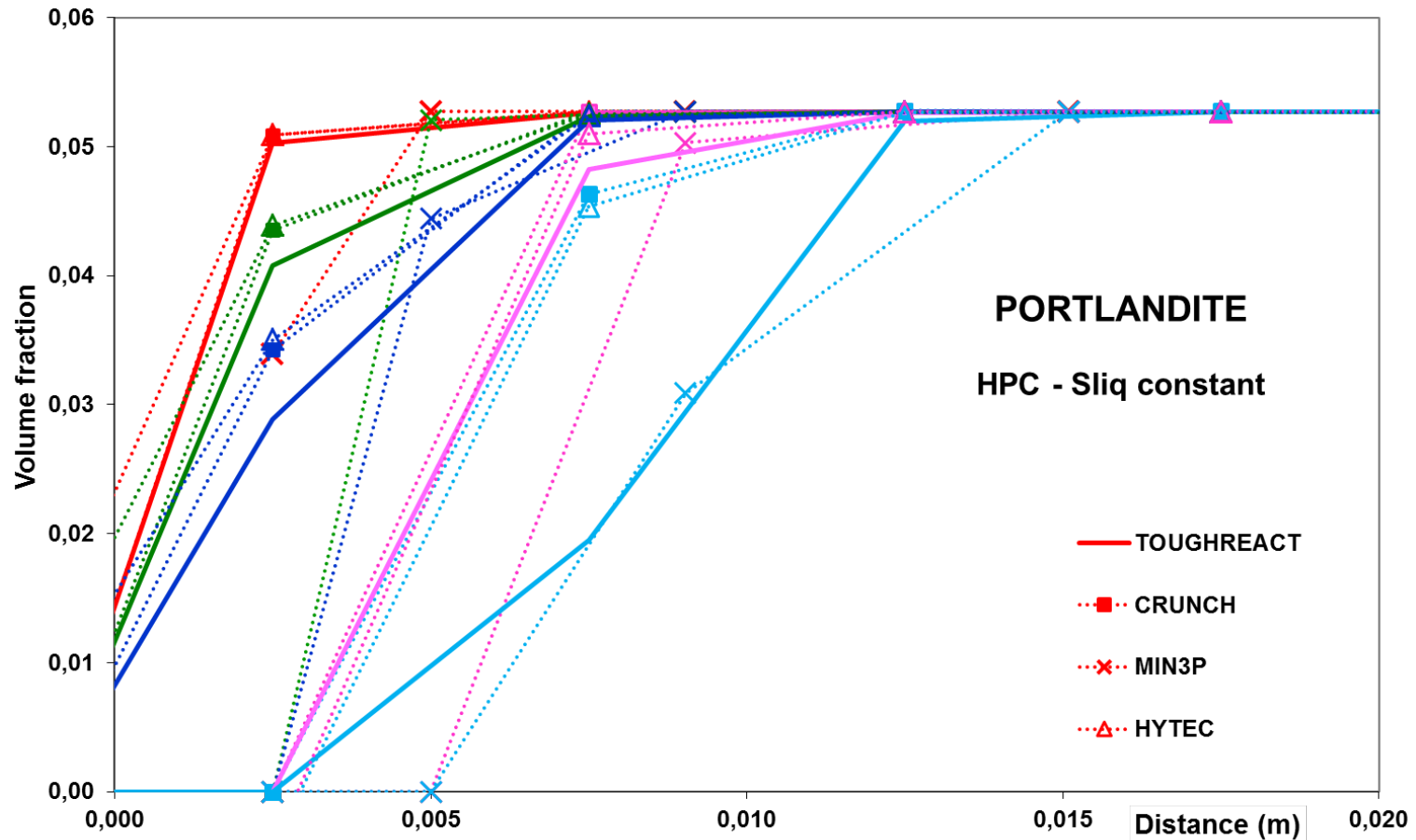
$$D_{eff} = D_0 \omega^a S_l^b$$



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

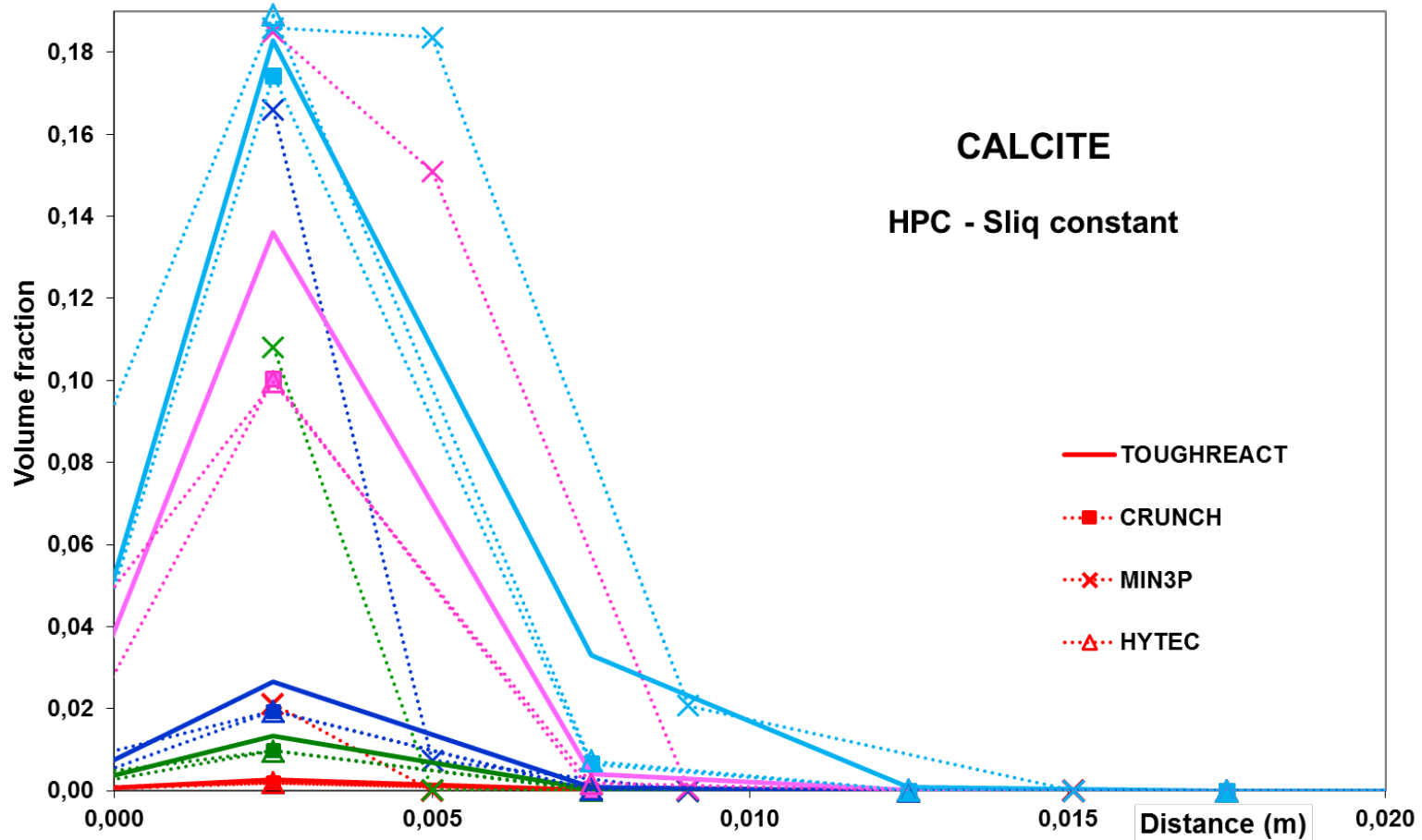


COMPONENT 2B: CONCRETE CARBONATION AT CONSTANT S_L



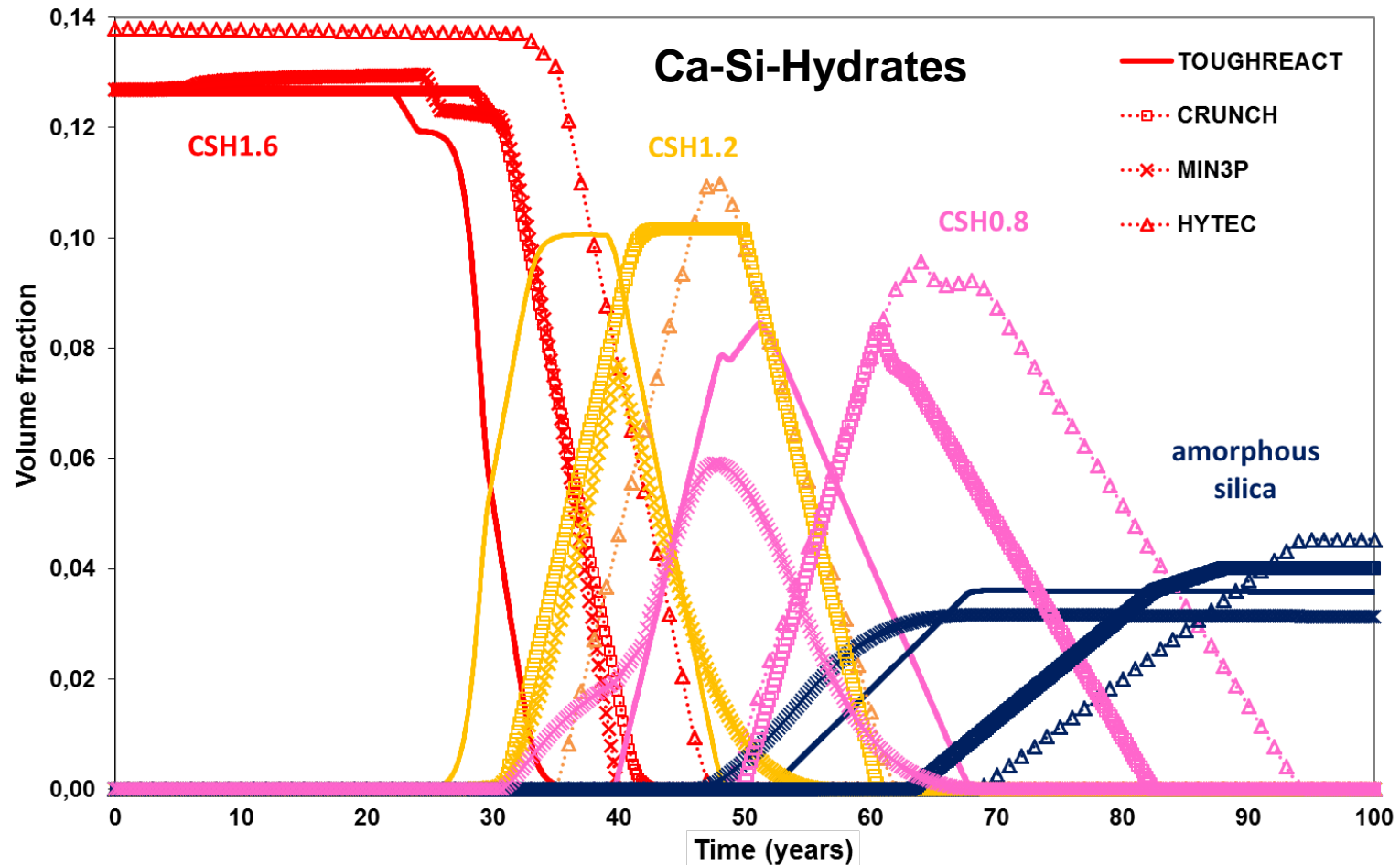
Carbonation front is similar, but the size of grid cells limits precise comparison

COMPONENT 2B: CONCRETE CARBONATION AT CONSTANT S_L



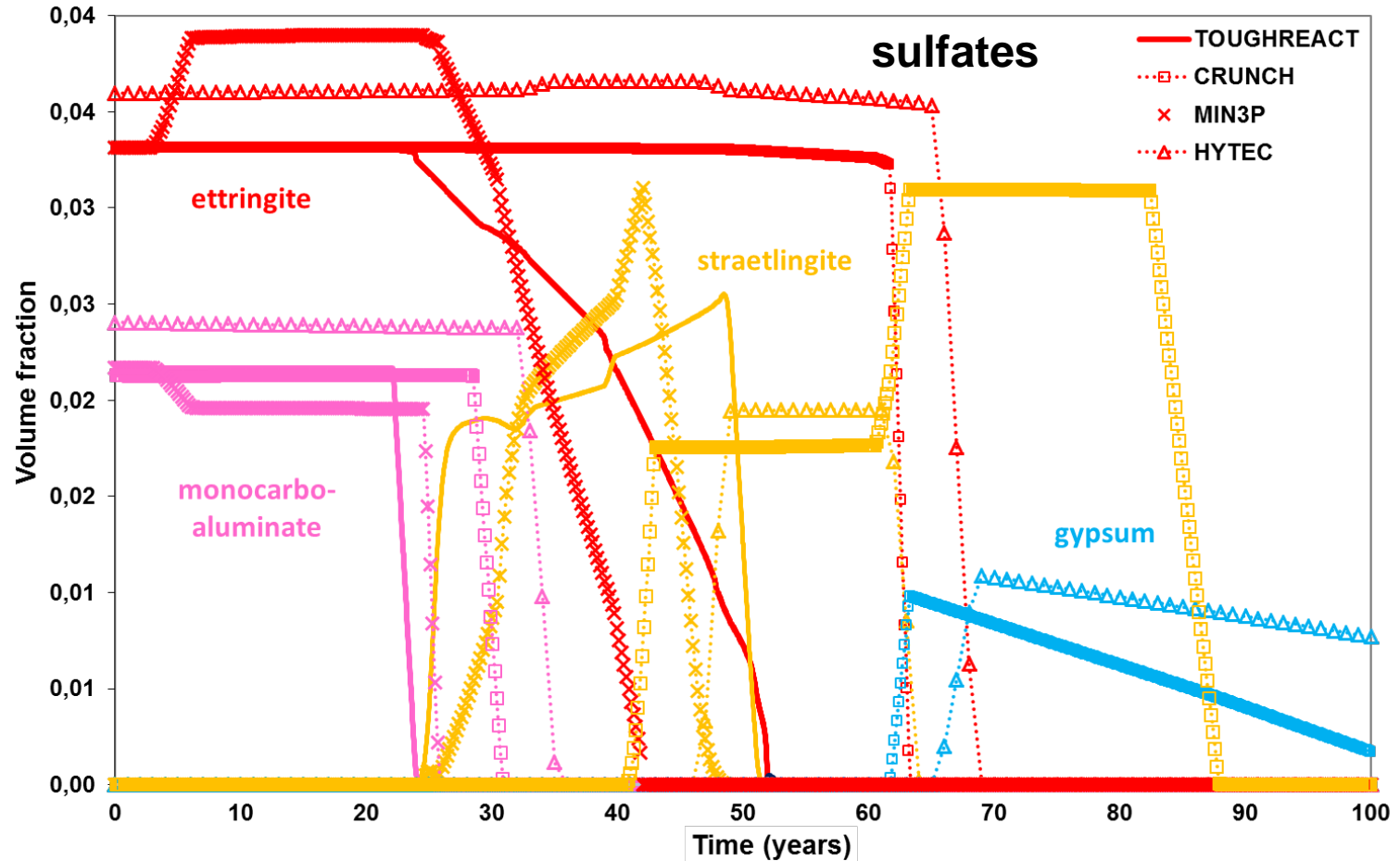
Calcite precipitation front is similar (MIN3P a little ahead of time/distance)

COMPONENT 2B: CONCRETE CARBONATION AT CONSTANT S_L



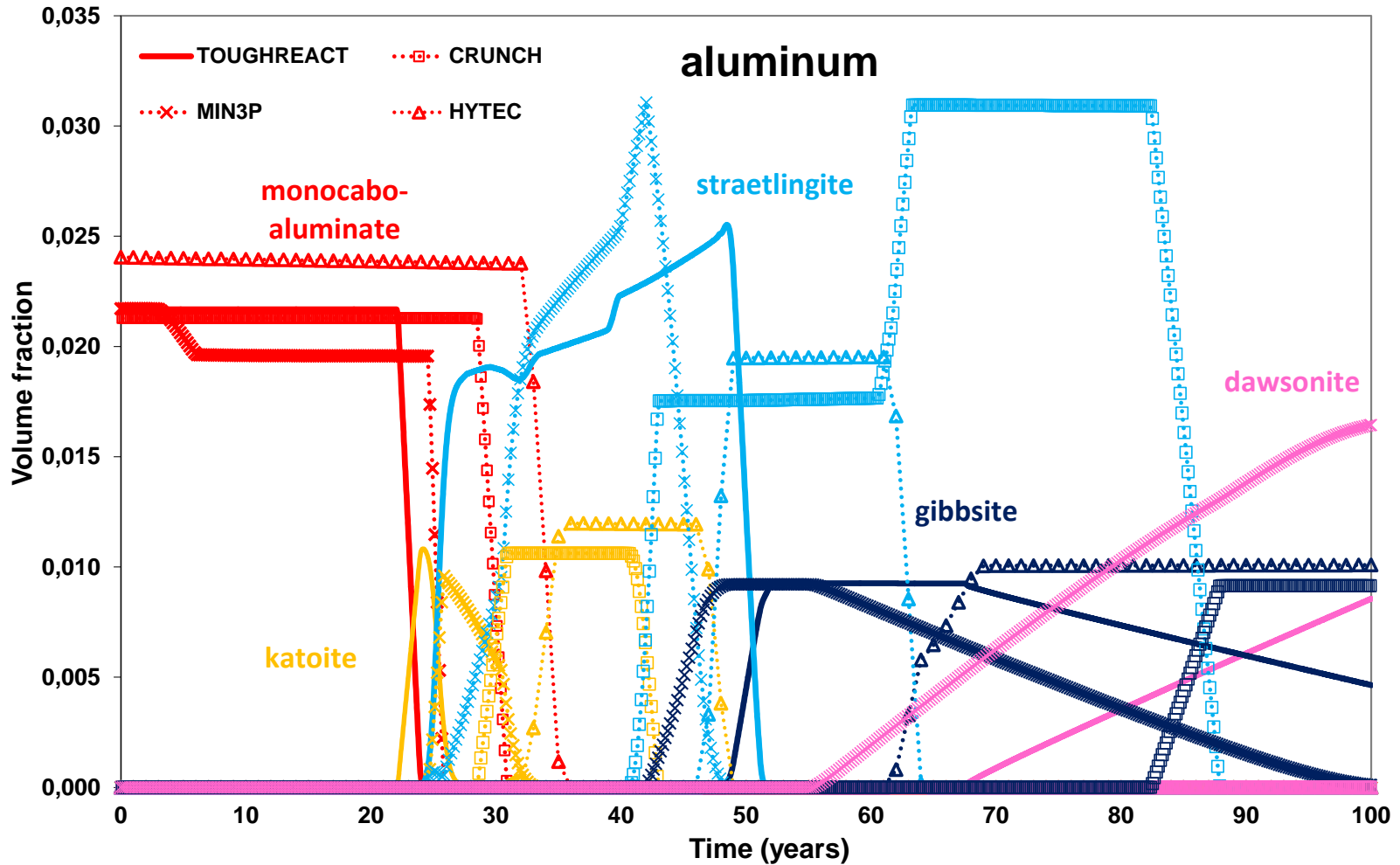
Same mineral paragenesis but timing not exactly the same for all codes

COMPONENT 2B: CONCRETE CARBONATION AT CONSTANT S_L



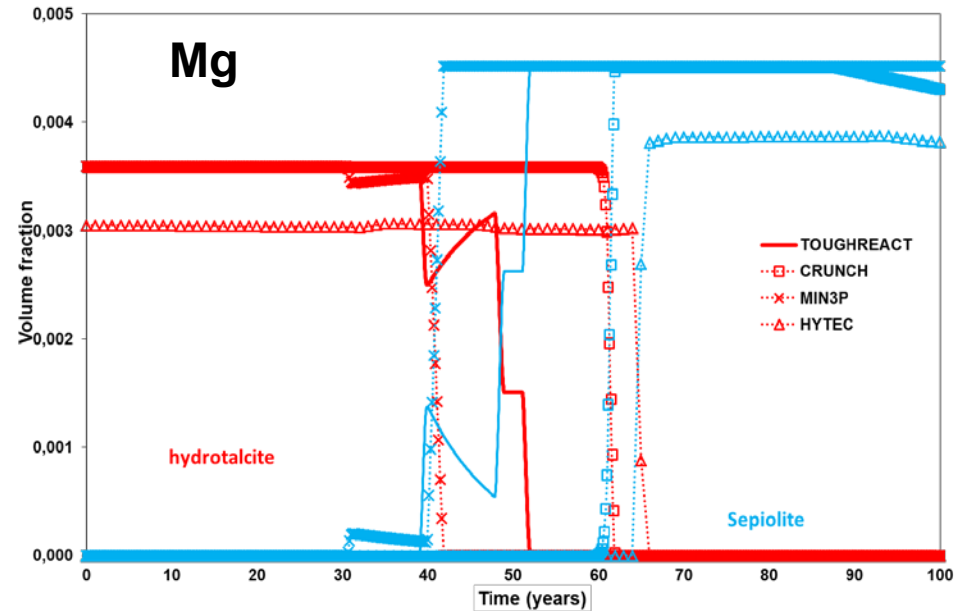
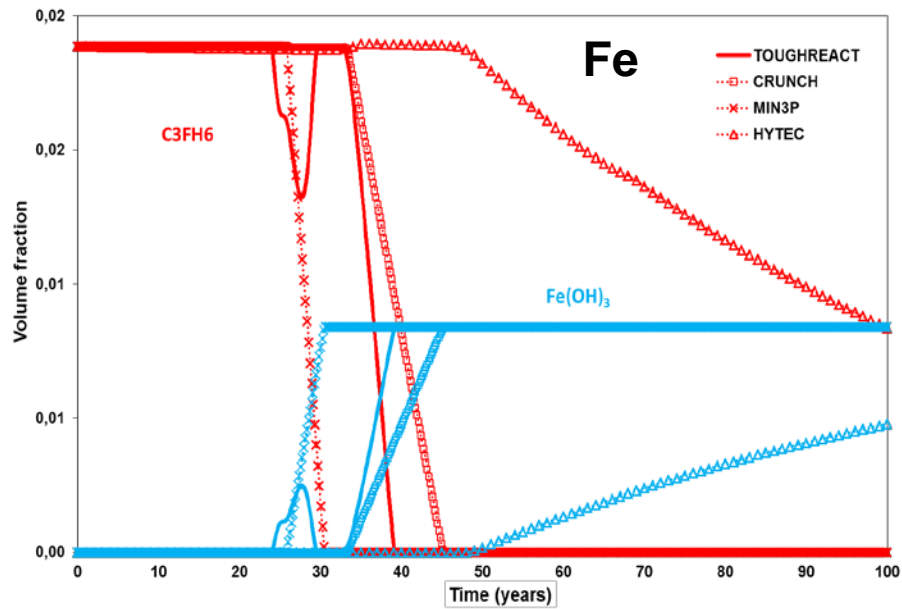
Precipitation of gypsum in the simulation with Crunchflow and Hytec

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

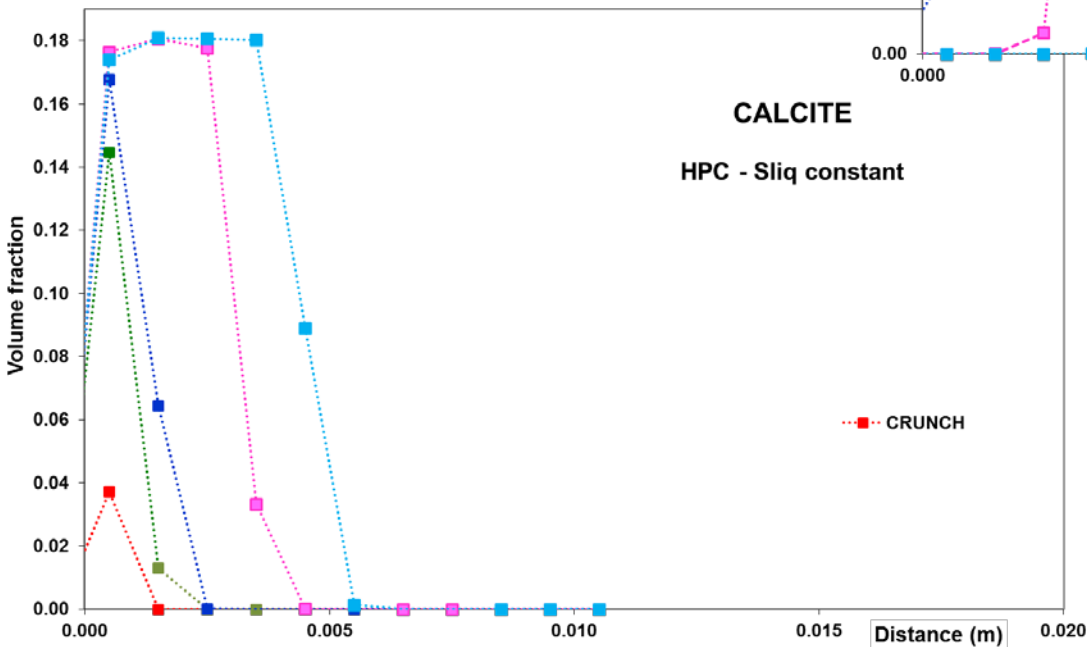
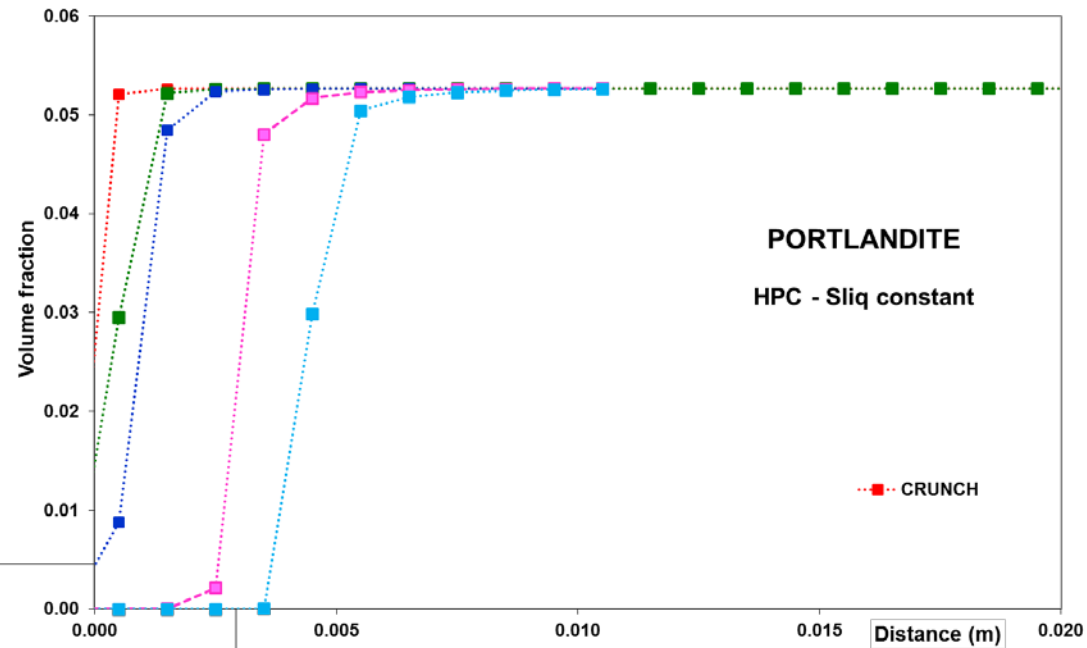


Same mineral paragenesis but timing not exactly the same for all codes

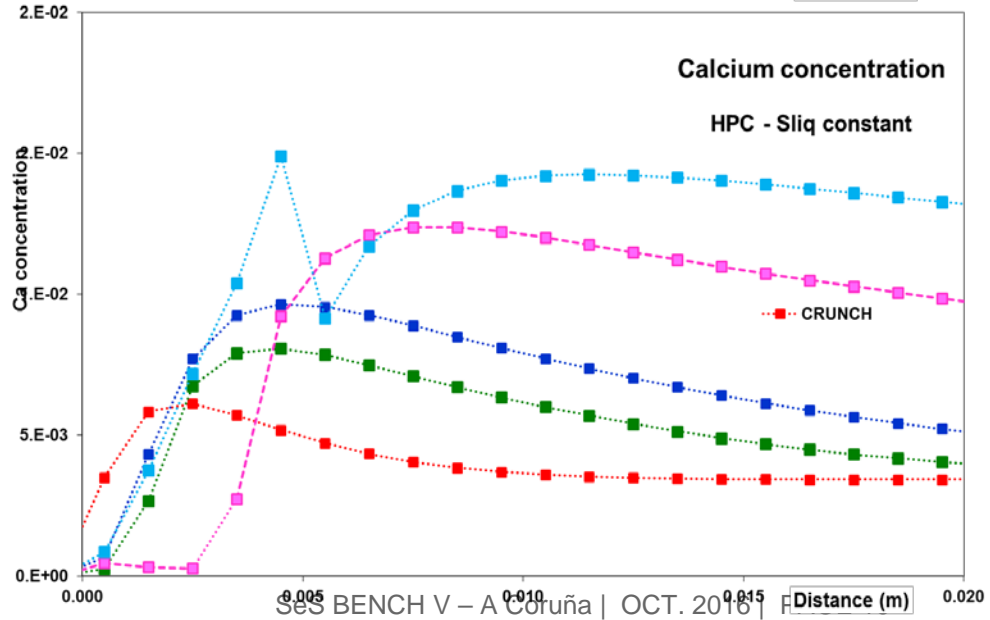
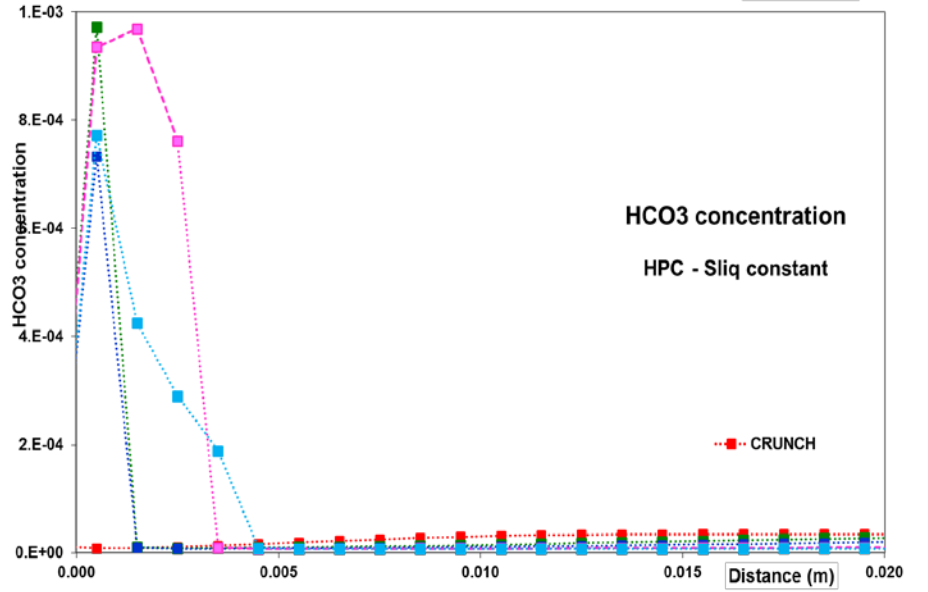
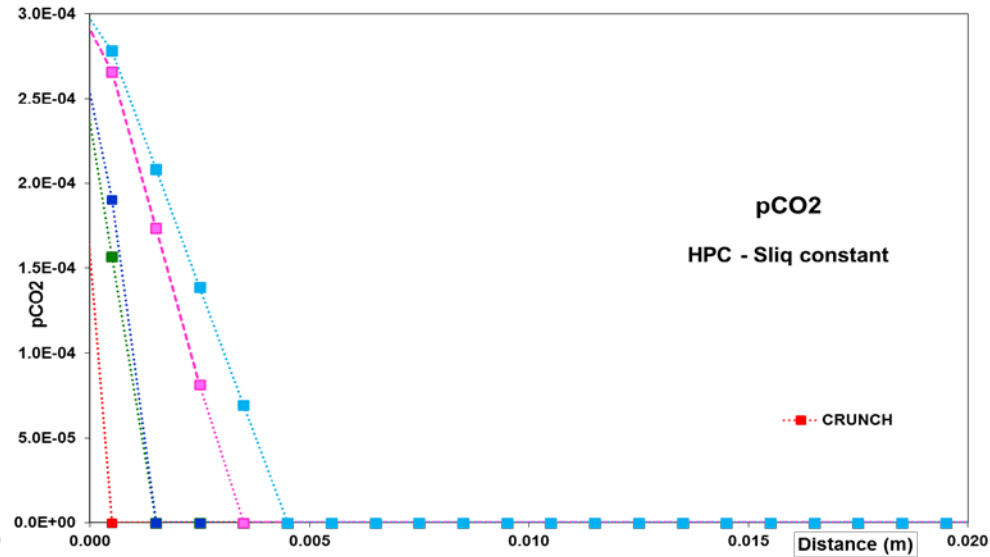
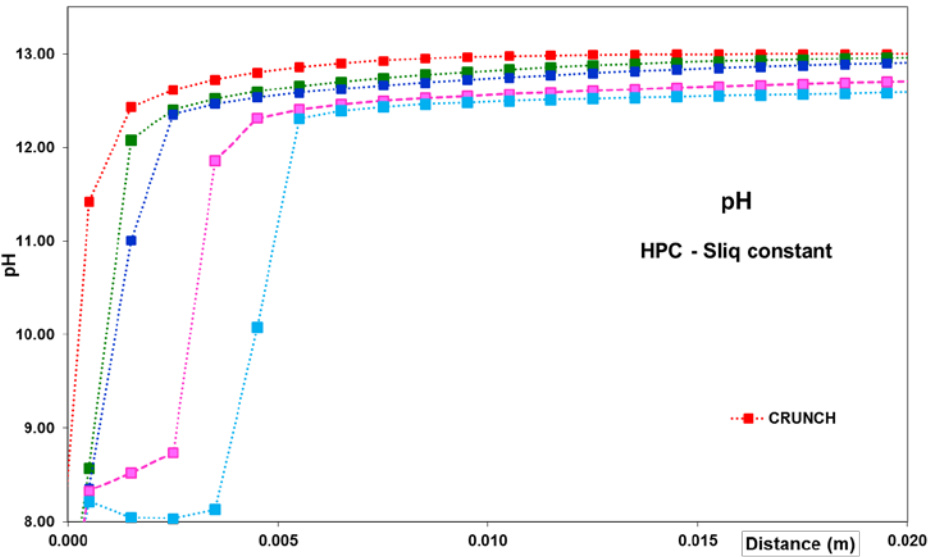
COMPONENT 2A: PORTLANDITE-CALCITE SYSTEM AT CONSTANT S_L

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 !

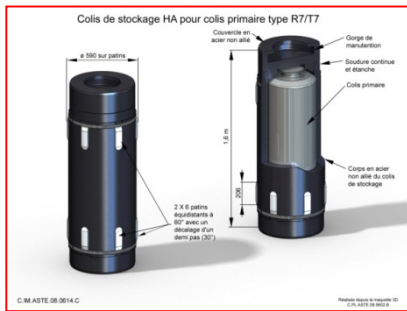
- ✓ Component 2a with simplified chemistry

- ✓ Component 3 with fully coupled drying+carbonation only with Toughreact

- ✓ New component : variable porosity?

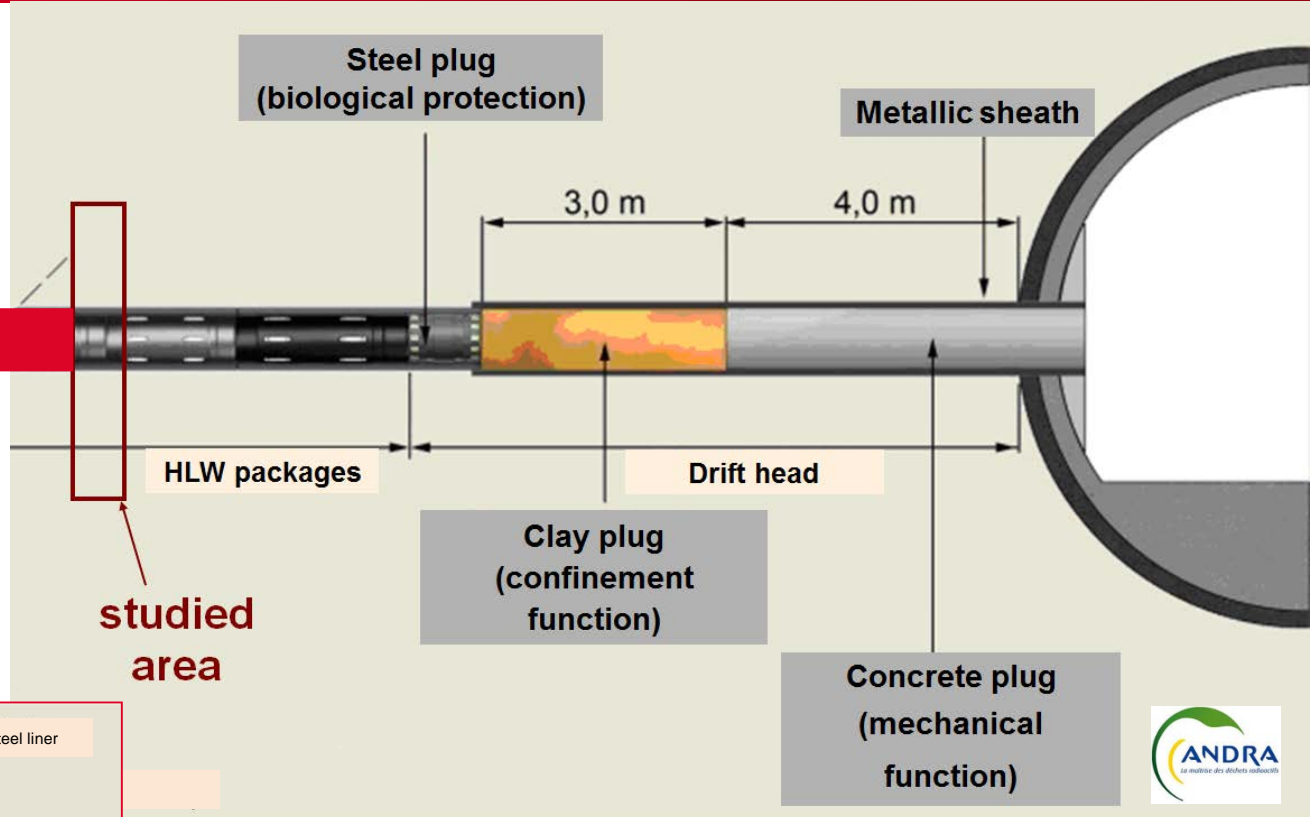
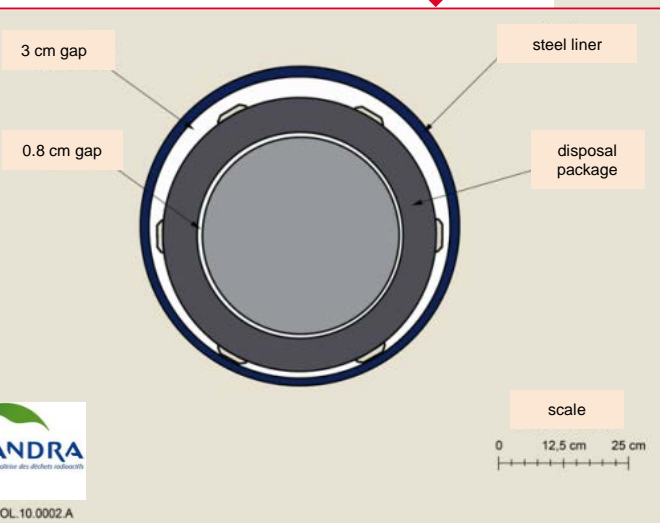
**Glass & steel
corrosion and
redox control
in claystones**

HLW DISPOSAL CELL



Vitrified waste packages

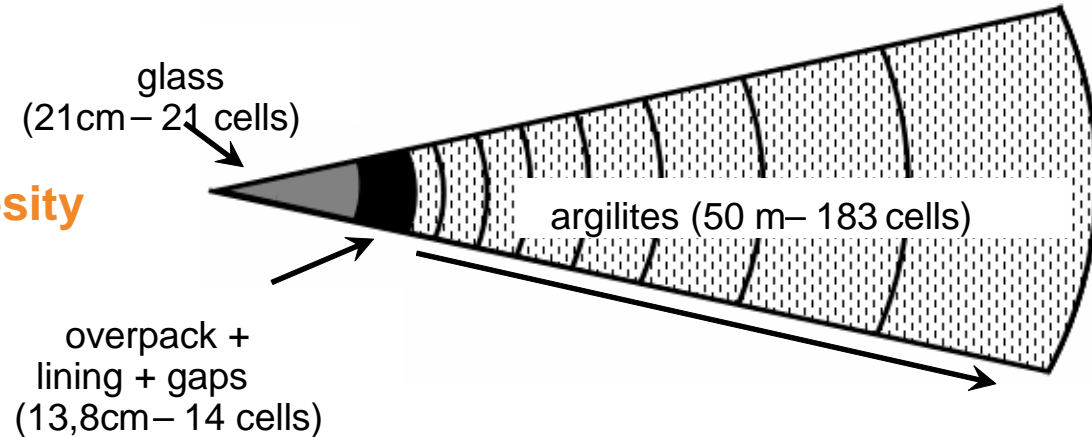
Cross section



- 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:

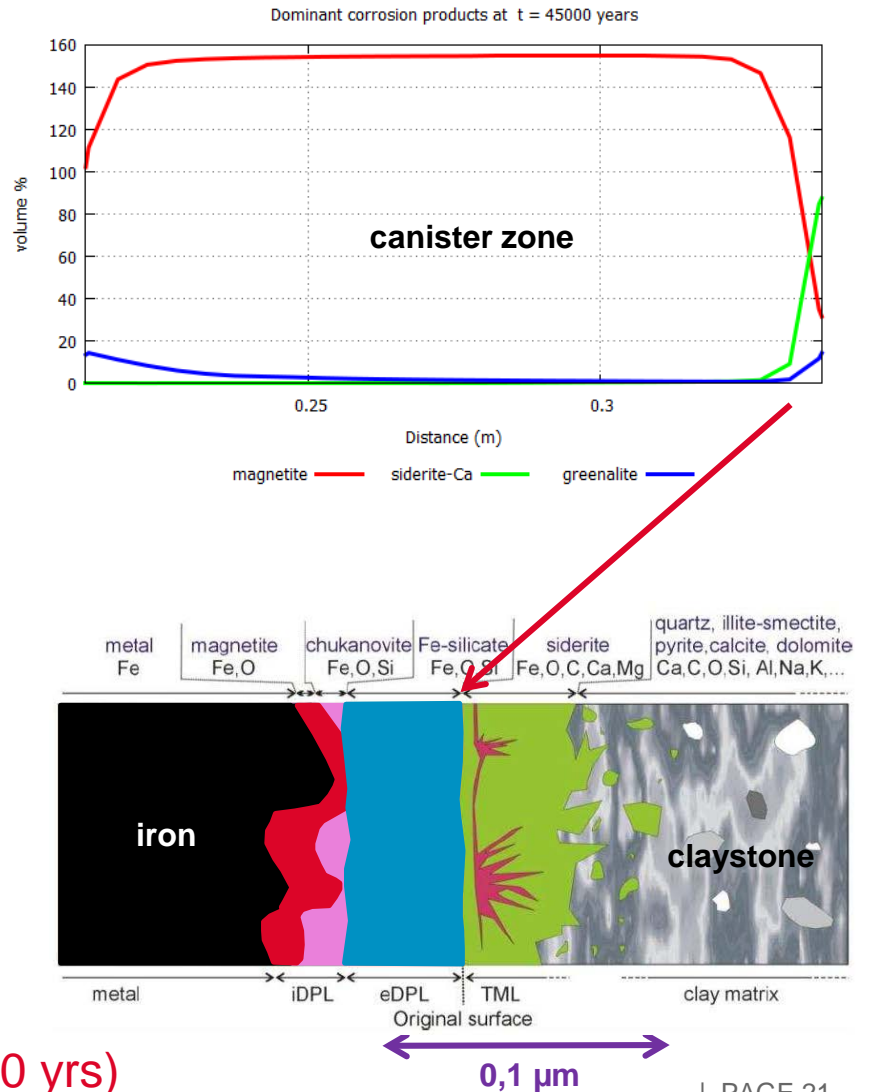
- highly reactive system
(strong pH and redox perturbation)
- complex geochemical system
(15 chemical elements, 80 aqueous species, 60 minerals)

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

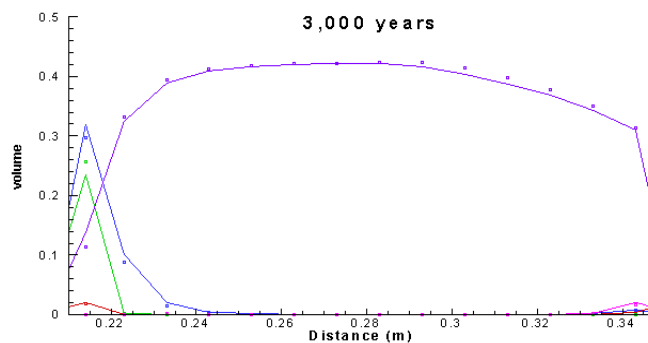
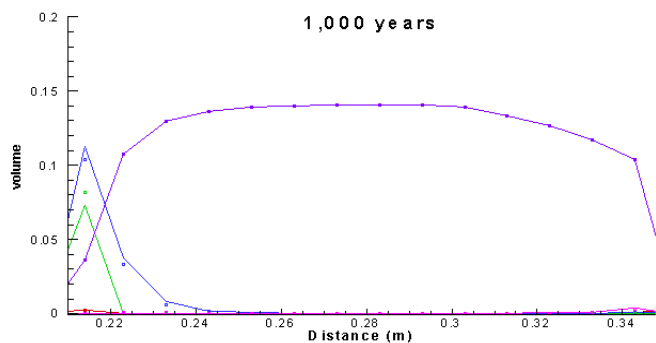
→ more phenomenological model for corrosion

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

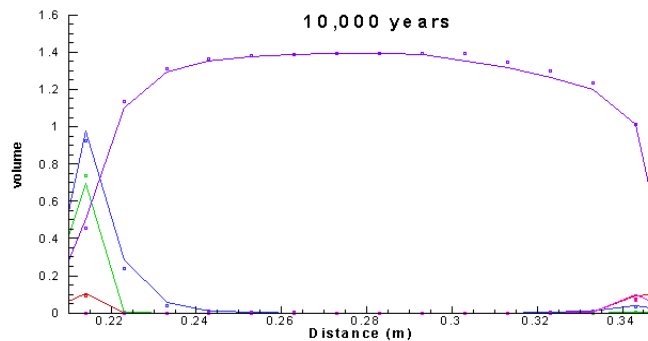
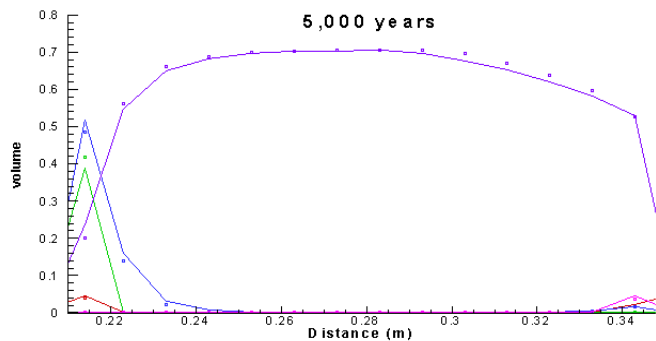


COMPONENT 1: RESULTS IN THE BASE CASE

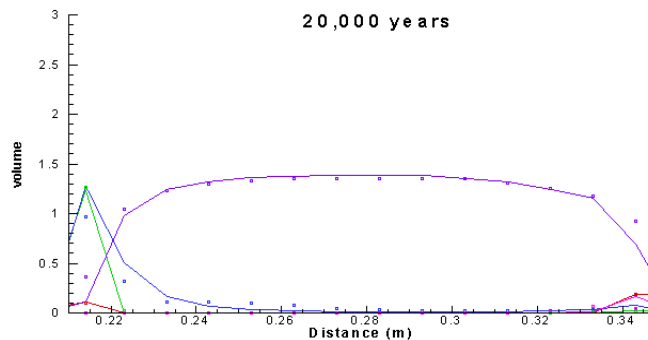
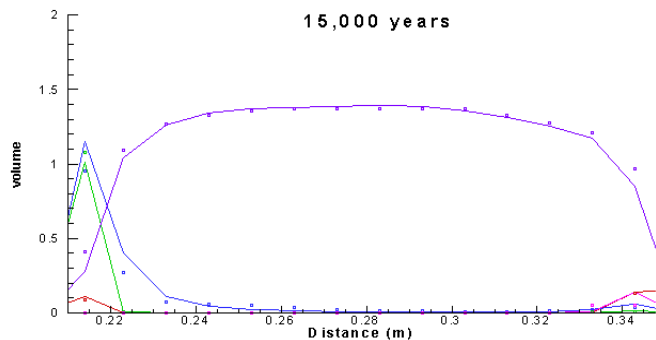
ONLY 2 CODES : MIN3P-Crunchflow (a very good agreement is obtained!) ...



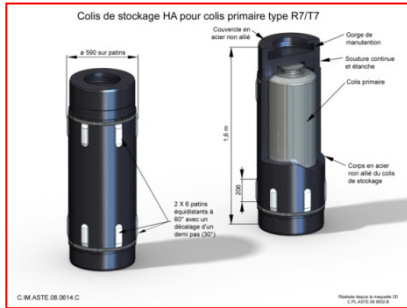
in the iron zone



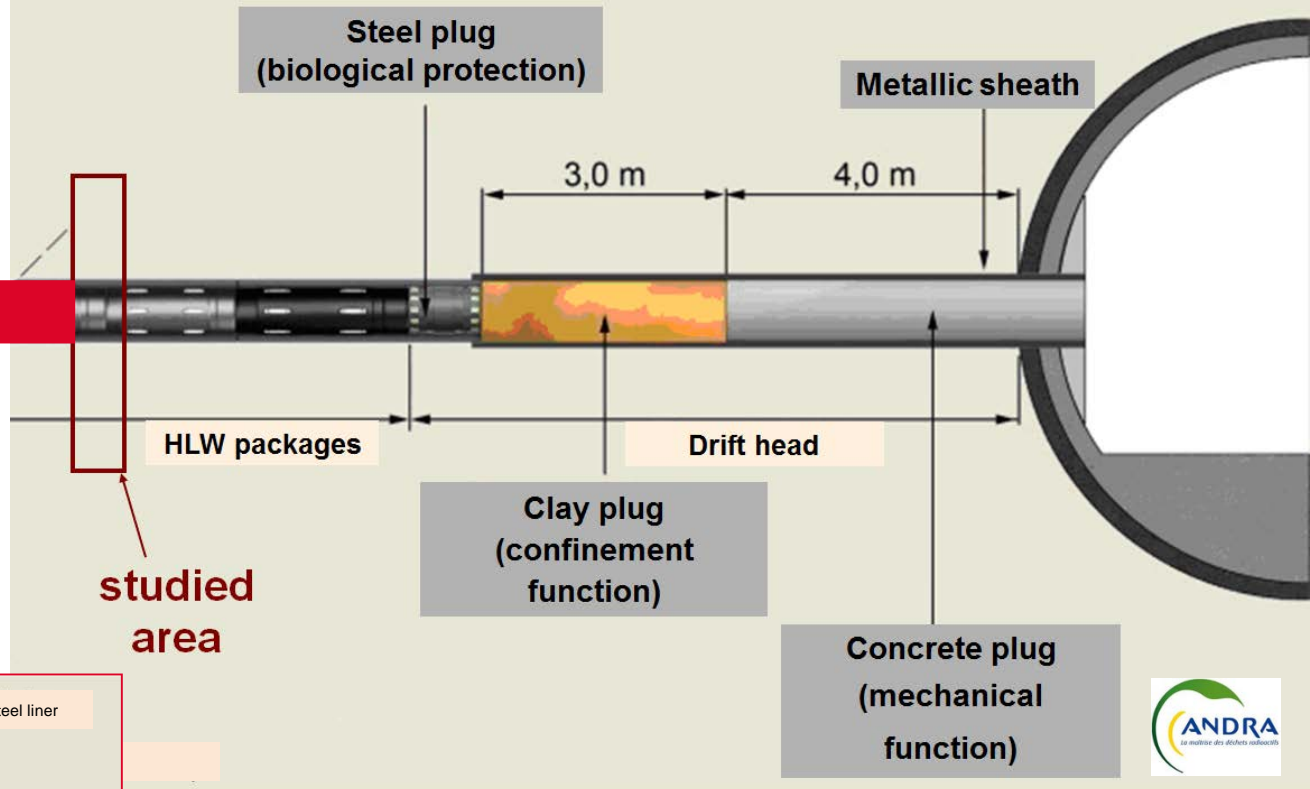
- Daphnite_14A - crunchflow
- Fe-Saponite-Na - crunchflow
- Greenalite - crunchflow
- Magnetite,beta - crunchflow
- Pyrrhotite-alpha - crunchflow
- - Daphnite_14A - MIN 3P
- - Greenalite - MIN 3P
- - Fe-Saponite-Na - MIN 3P
- - Pyrrhotite-alpha - MIN 3P
- - Magnetite,beta - MIN 3P



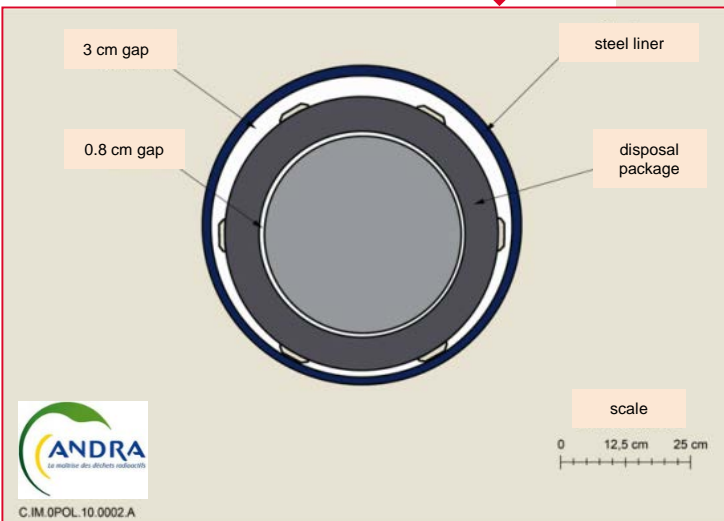
CORROSION IN HLW DISPOSAL CELL



Vitrified waste packages



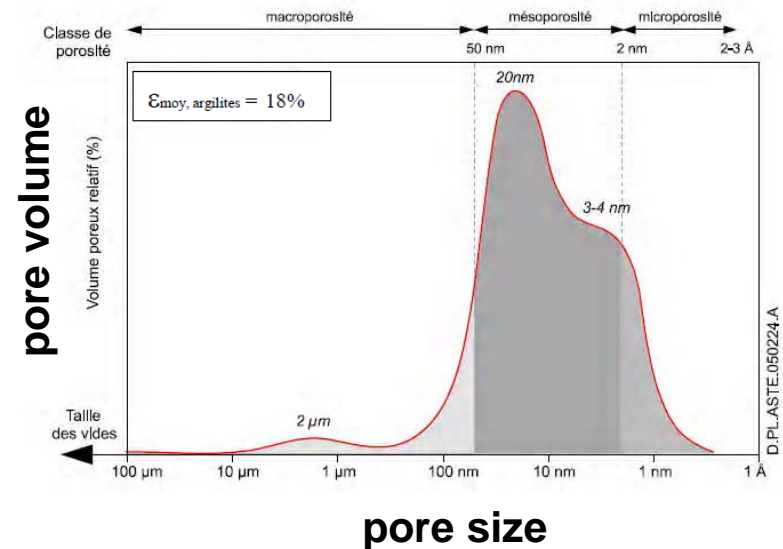
Cross section



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

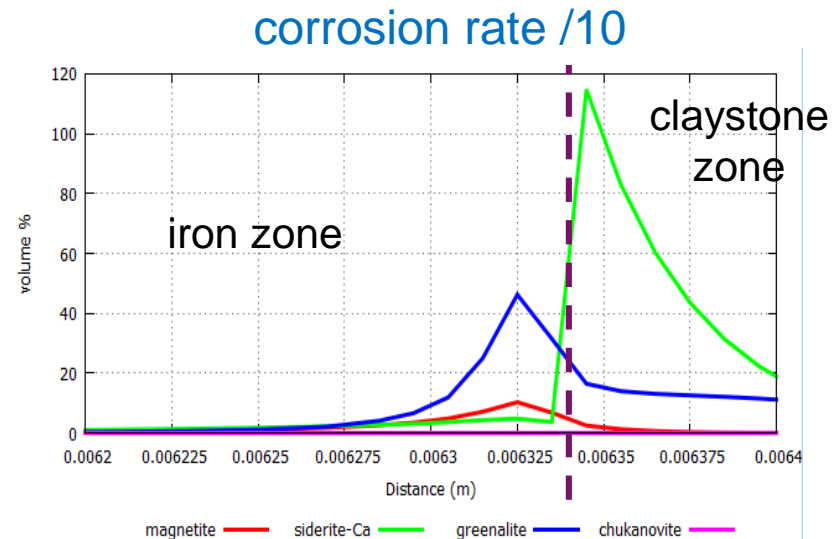
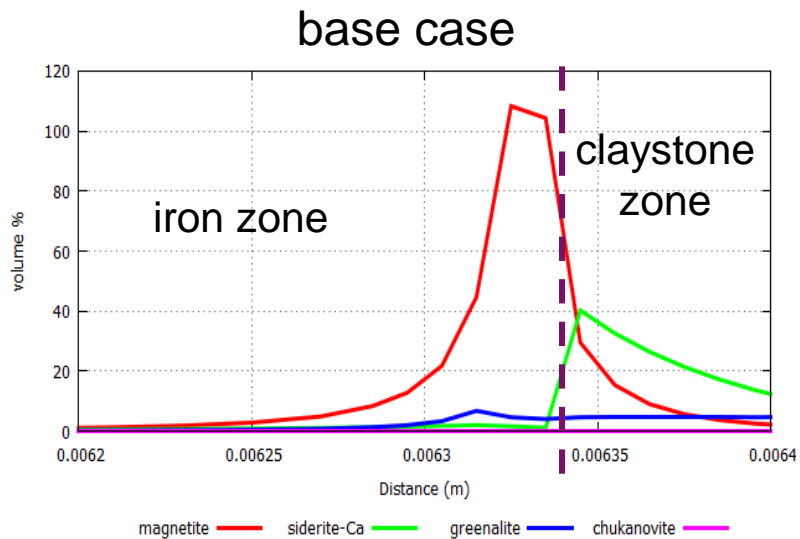
- reactivity of H_2 in claystones
(in tiny 20 nm connected pores)
 - only at interfaces in repository
 - redox control in claystones?
 - RN sorption/migration?
 - porosity clogging

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



✓ Corrosion in reactive transport codes

- ✓ changes in pH and Eh occur through:

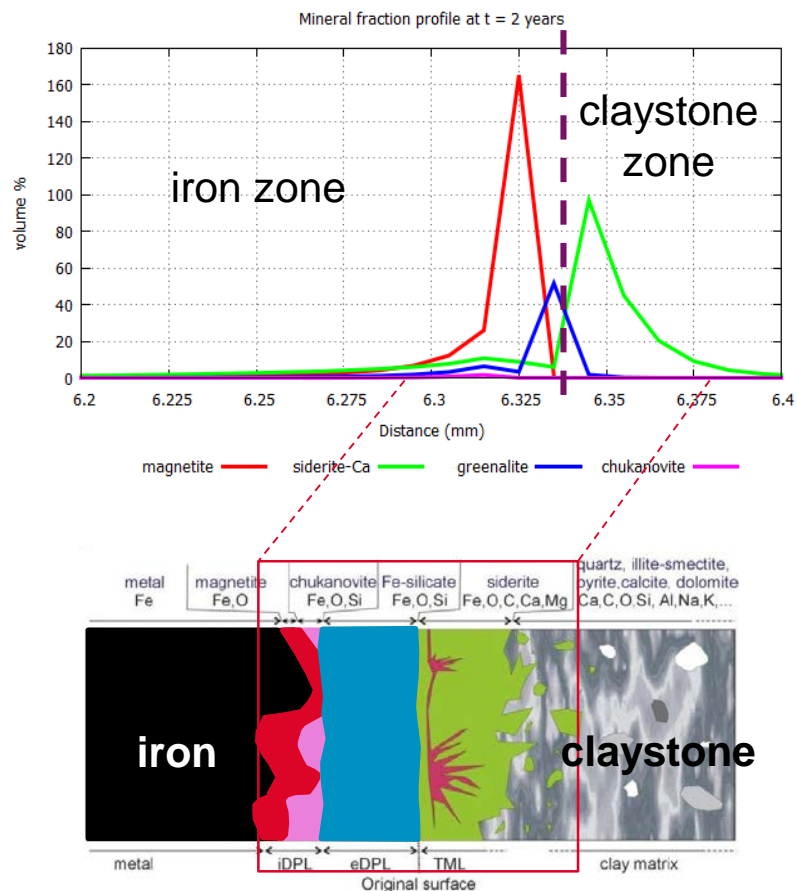


STEEL CORROSION “GEOCHEMICAL” REACTION

... 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



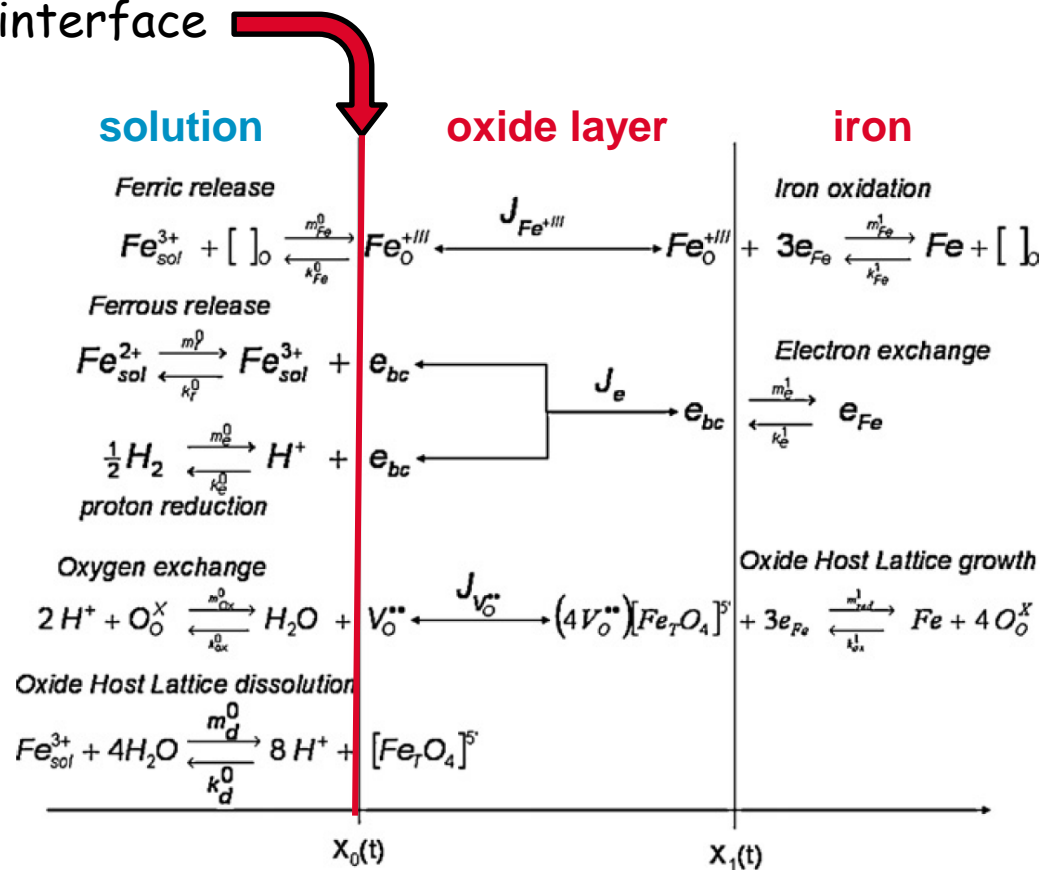
from Schlegel et al. 2014

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, H₂)?
 - ✓ use mineral reaction rates (corrosion and oxide layer precipitation/dissolution)?
 - ✓ use fluxes for Fe²⁺ and Fe³⁺ and aqueous kinetics?

THANK YOU FOR YOUR ATTENTION

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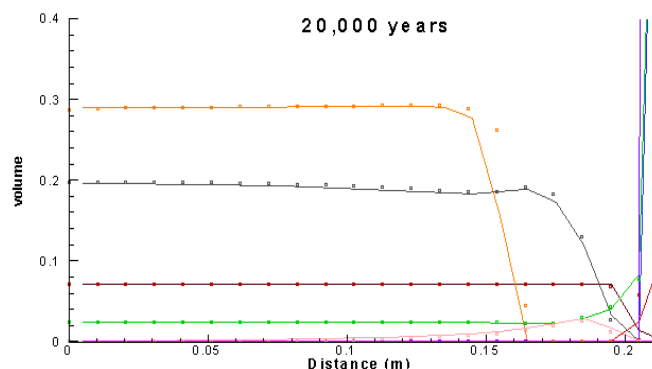
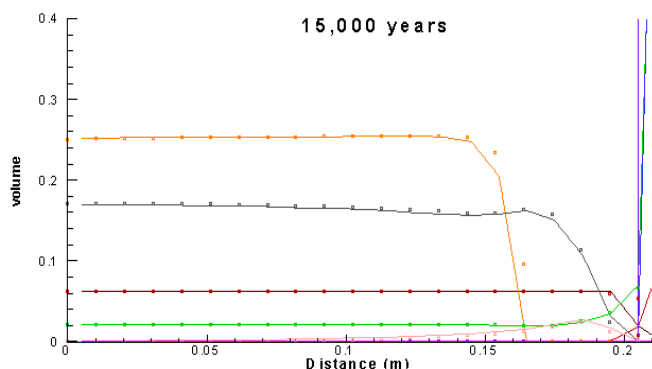
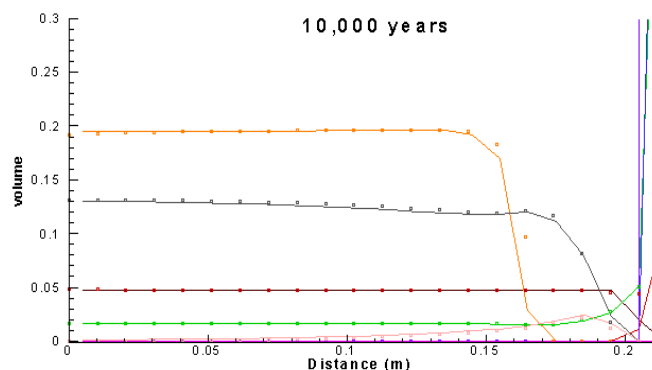
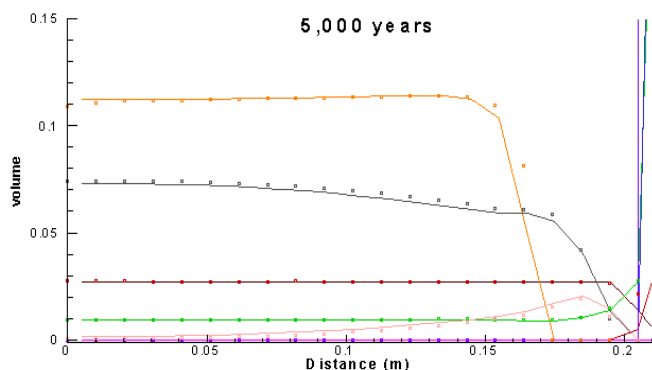
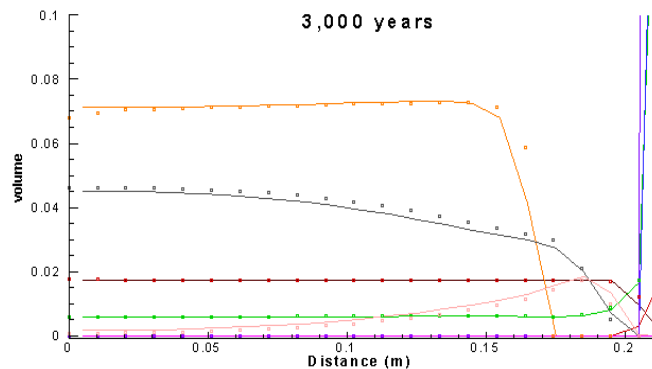
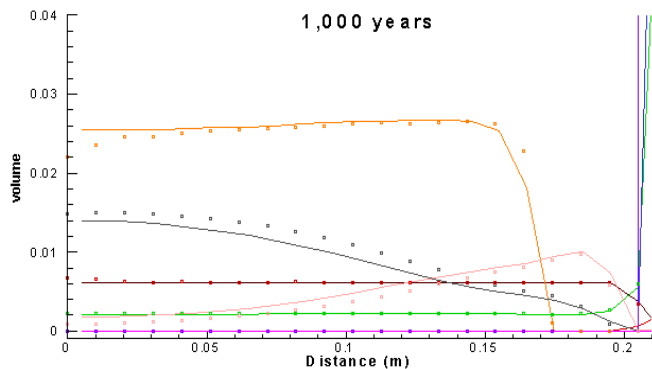
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Direction de l'Energie Nucléaire
Département des Technologies
Nucléaires
Service de Modélisation des Transferts
et de Mesures Nucléaires

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

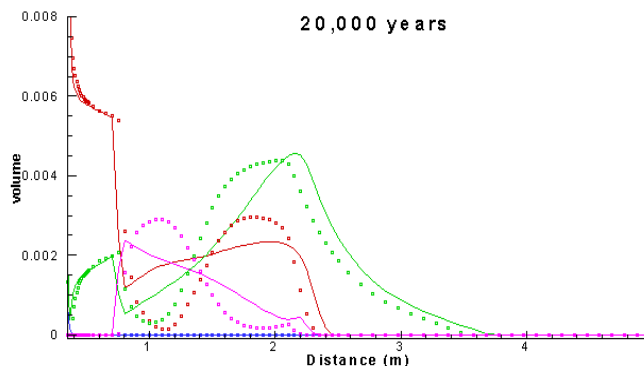
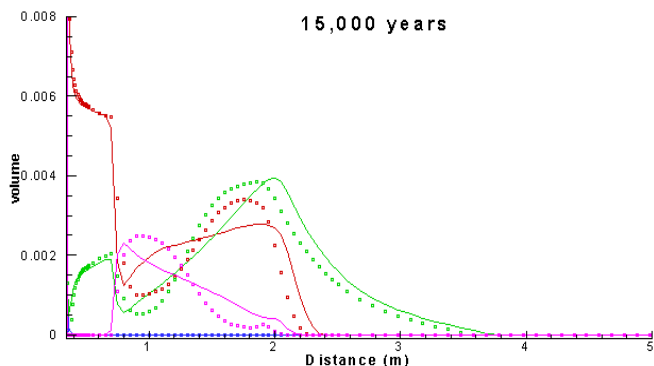
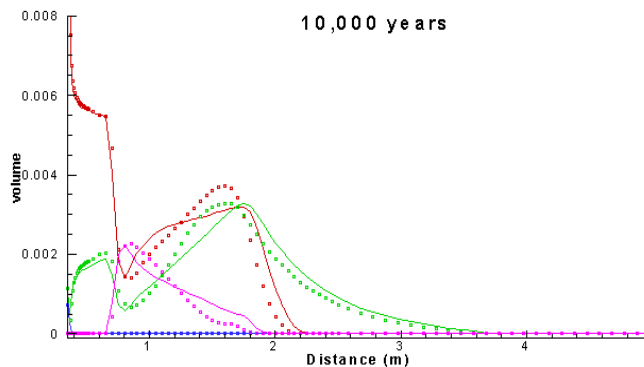
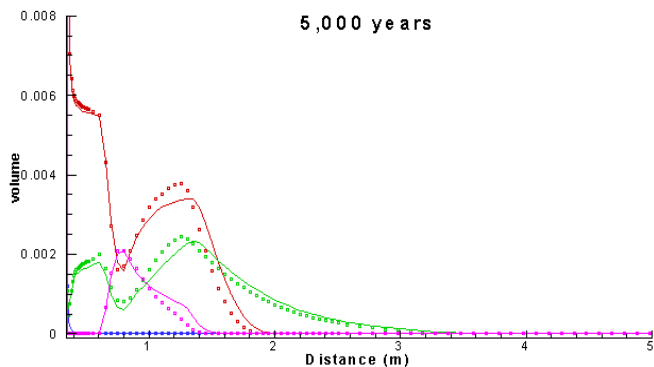
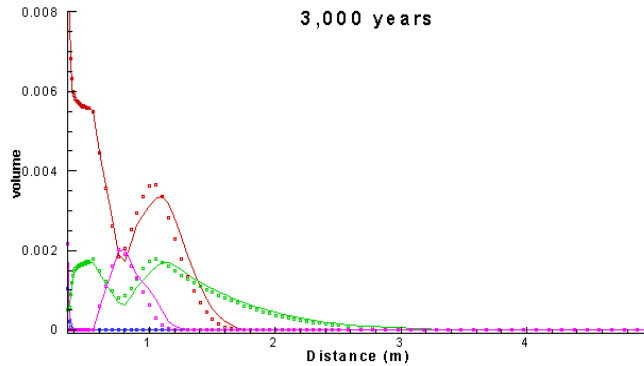
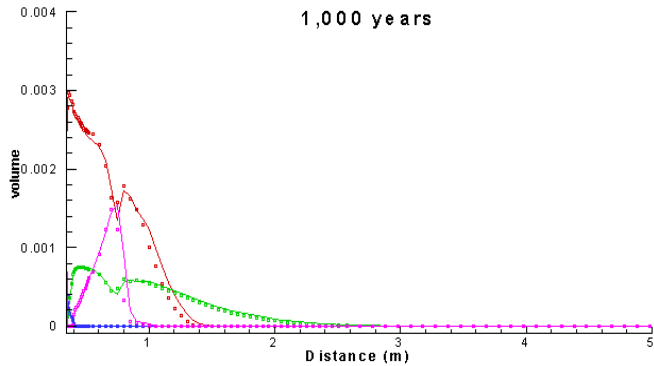
RESULTS IN THE BASE CASE (3)

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