Reactive transport modeling of leaching tests and long-term processes applied to cementitious waste disposal

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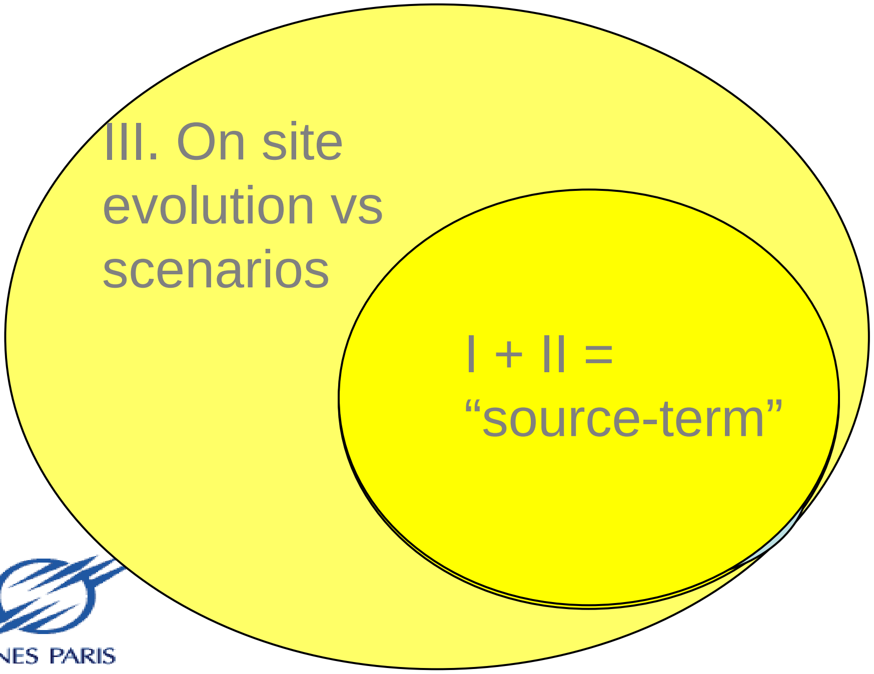
Cementitious materials for waste treatment, disposal,
remediation and decommissioning workshop, Dec. 12-14
(2006), SNRL (USA)

Context and objectives

- **Performance AND environmental impact assessment of waste disposal (or recycling scenarios)**
  - Dynamic leaching tests to better characterize the cementitious waste long-term evolution
  - Understanding of leaching mechanisms to extrapolate the laboratory results to engineered systems (decommissioning, disposal) or waste/environment interactions (disposal, recycling)



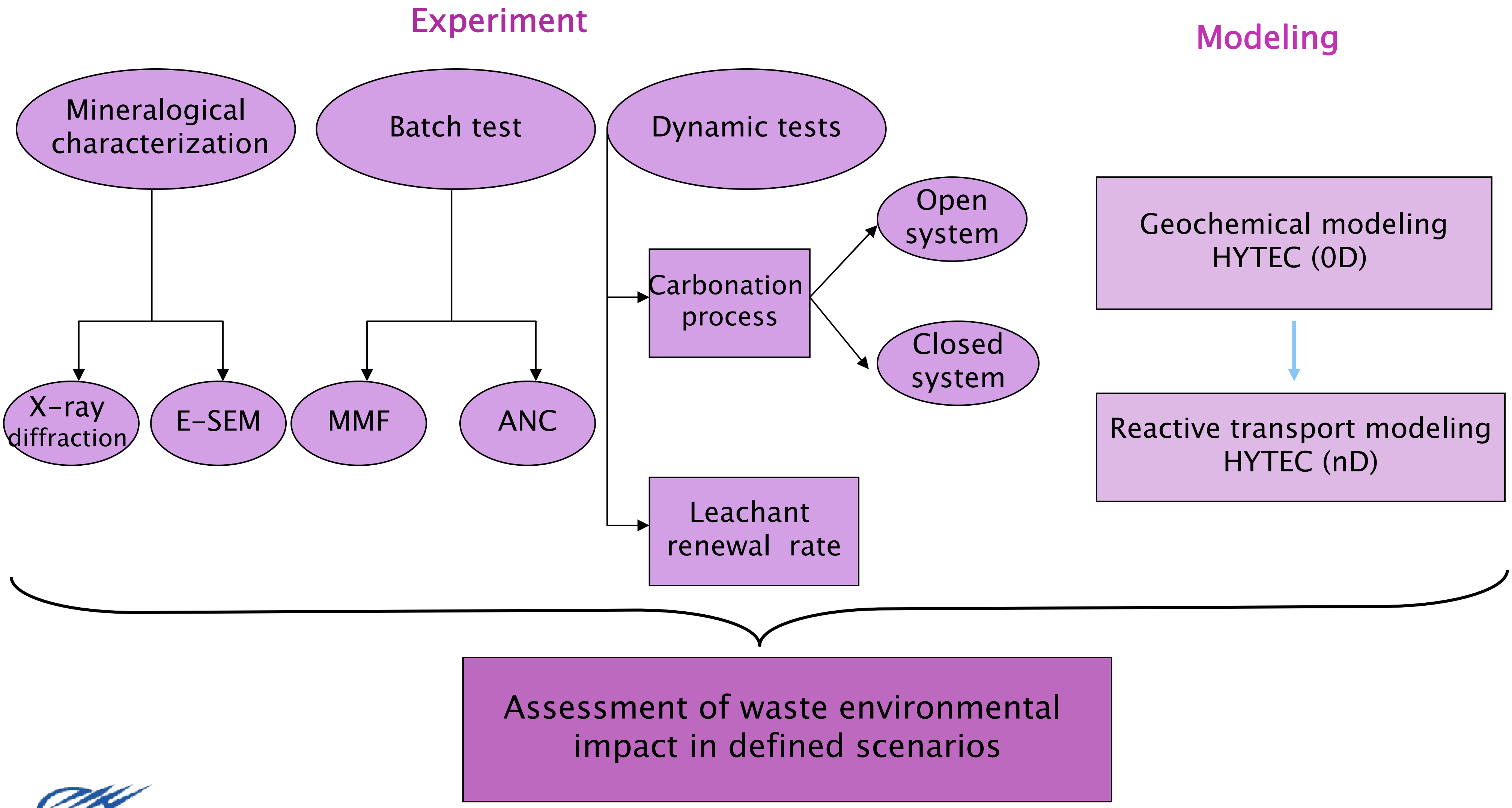
III. On site evolution vs scenarios

I + II = "source-term"

- **Needs for a "common" modeling approach and code applied to different scales, as mechanistic as possible**
  - Reactive transport codes are good candidates

- I + II: *Waste Management (2006), in press*
- III: *J. Hazardous Mater. (2006), in press*

Source-term characterization



Experiment

Modeling

Mineralogical characterization

Batch test

Dynamic tests

X-ray diffraction

E-SEM

MMF

ANC

Carbonation process

Open system

Closed system

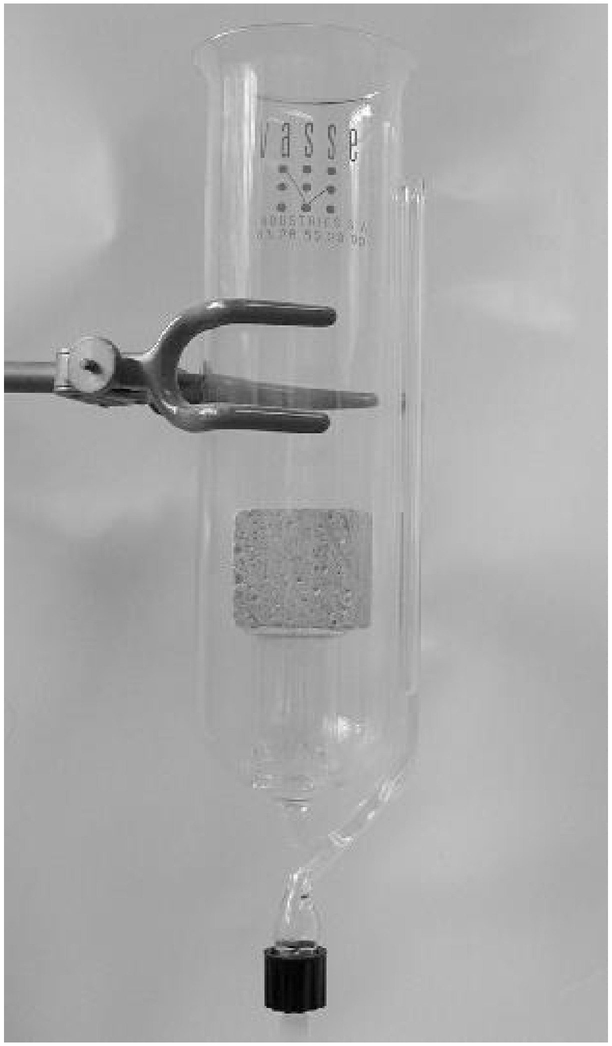
Leachant renewal rate

Geochemical modeling HYTEC (0D)

Reactive transport modeling HYTEC (nD)

Assessment of waste environmental impact in defined scenarios

Solidified/stabilized waste



- Solidification recipe:
  - 1/4 CEM-I (OPC)
  - 3/4 siliceous sand
  - Pb (1%)

- Porous monolithic material:
  - 4 x 4 x 4 cm^3
  - $\omega \sim 0.15$

    (75% pore size < 1 µm)
  - Deff $\sim 3\ 10^{-12}\ m^2/s$

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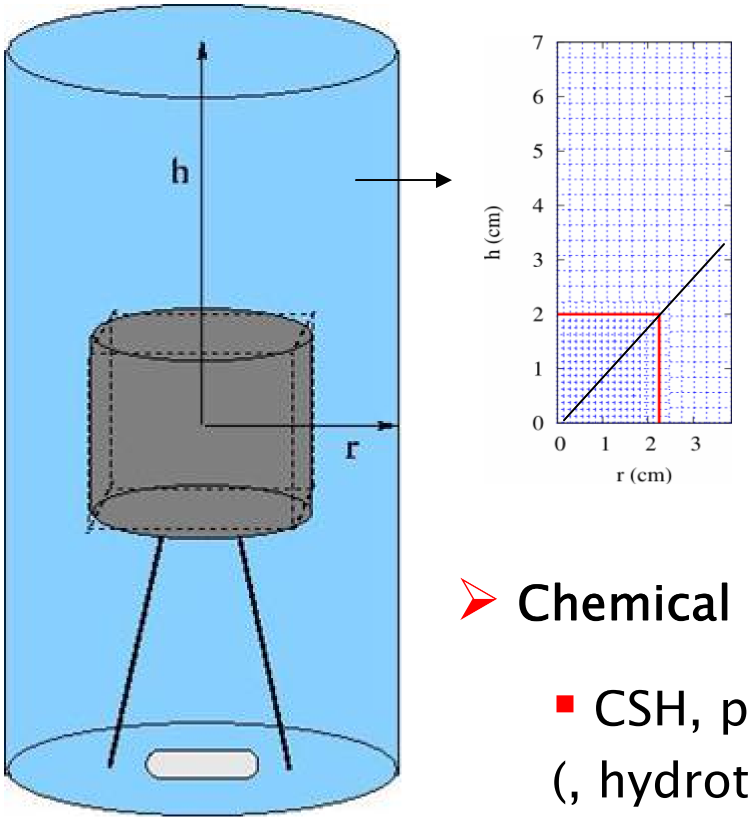
Modeling features



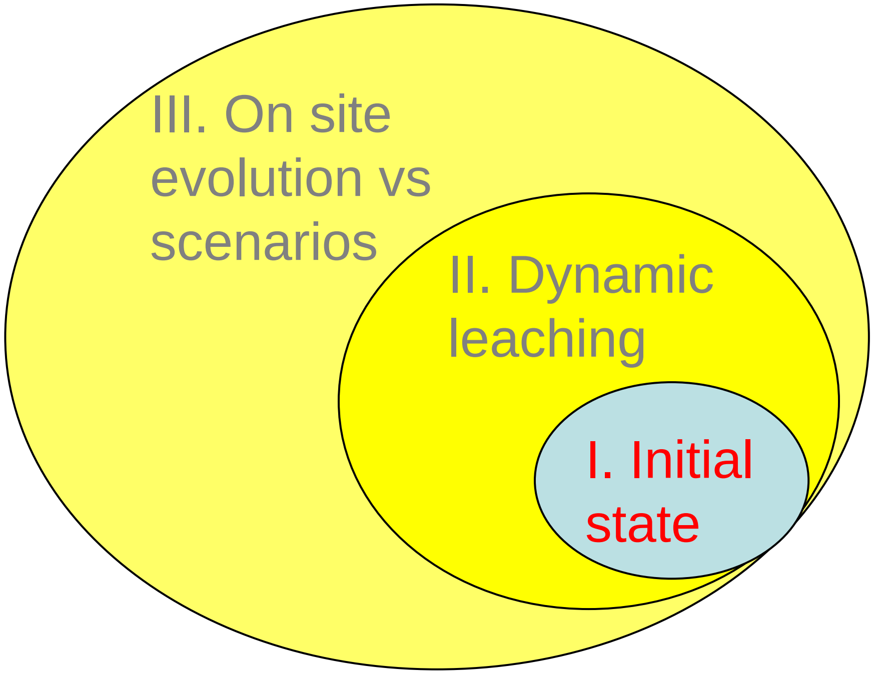
- **Reactive transport code HYTEC**:
  - 3D-cylindrical geometry (REV)
  - $$\frac{\partial \omega c_i}{\partial t} = \nabla(D_e.\nabla c_i) - \frac{\partial \omega \bar{c}_i}{\partial t}$$
  - feedback of chemistry on ω and D_e

$$D_e(\omega) = D_e(\omega_0)\left(\frac{\omega - \omega_c}{\omega_0 - \omega_c}\right)^m$$

  - closed (or open) conditions

- **Chemical model**:
  - CSH, portlandite, ettringite, Friedel’s salt (, hydrotalcite)
  - Pb in substitution in CSH 1.7
  - *OPC pore water chemistry (pH ~ 13.3)*
  - MINTEQ TDB + cement phases (+ sorption)

Stage 1



III. On site evolution vs scenarios

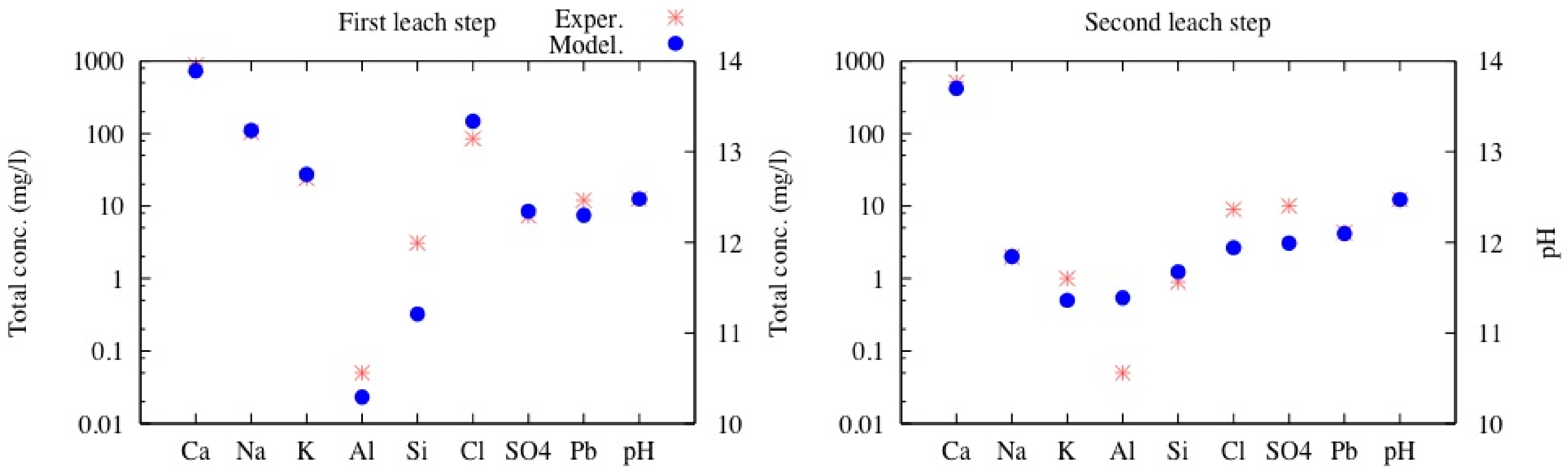
II. Dynamic leaching

I. Initial state

- ➢ Needs for a “common” modelling approach and code applied to different scales, as mechanistic as possible
  - ▪ Reactive transport codes are good candidates

Pore water and MMF batch test

L/S = 10 → L/S = 50



- Local thermodynamic equilibrium assumption with initial solid phases +

  Na, K, Cl (almost) conservative and adjusted from the MMF batch tests
- Fairly to very good experimental/modeling agreement
- Extraplation to ↘↘ L/S gives pore water chemistry

Calculated pore water chemistry

Calculated chemistry of pore water with considering the sorption of Na on CSH phases.

pH	13.3	
Na^+	8 800	mg/l
K^+	4 100	mg/l
Ca^{2+}	64	mg/l
Pb^{2+}	57	mg/l
Al^{3+}	0.08	mg/l
H_4SiO_4	99	mg/l
Cl^-	5 050	mg/l
SO_4^{2-}	1 250	mg/l

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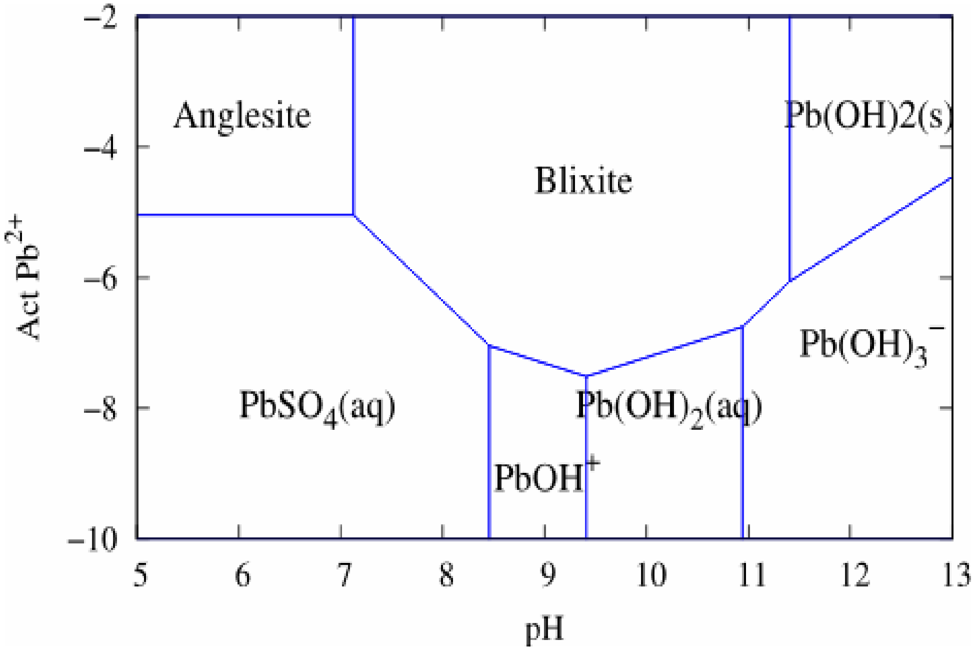
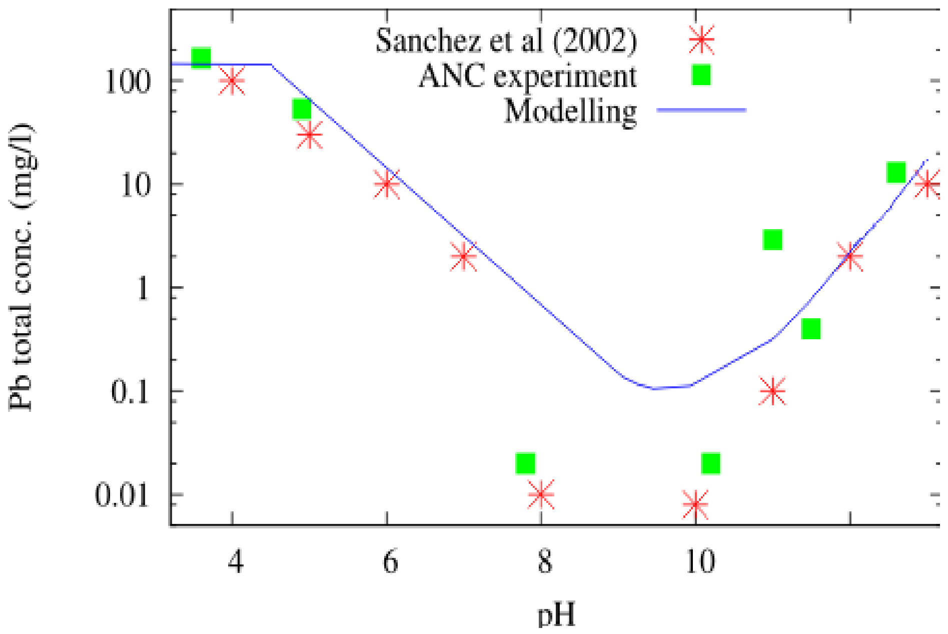
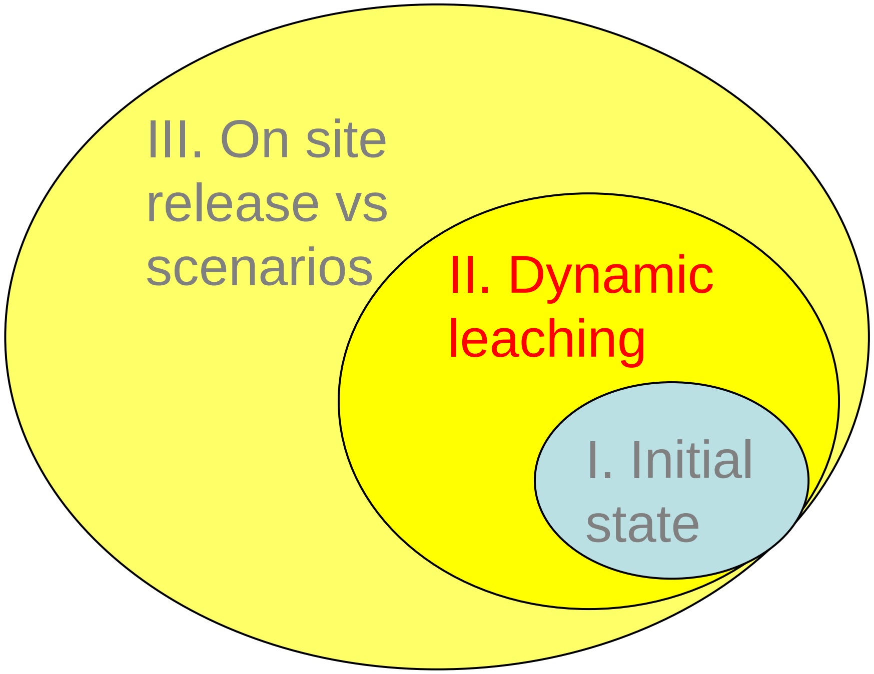
Lead solubility vs pH and ANC batch test





- Good at very good agreement, in particular the amphoteric properties, except for the lowest concentration
- Pb solubility would be controlled by hydroxide-like complexes and solid phases at alkaline pH and closed conditions, no matter Pb is substituted or sorbed on CSH ?

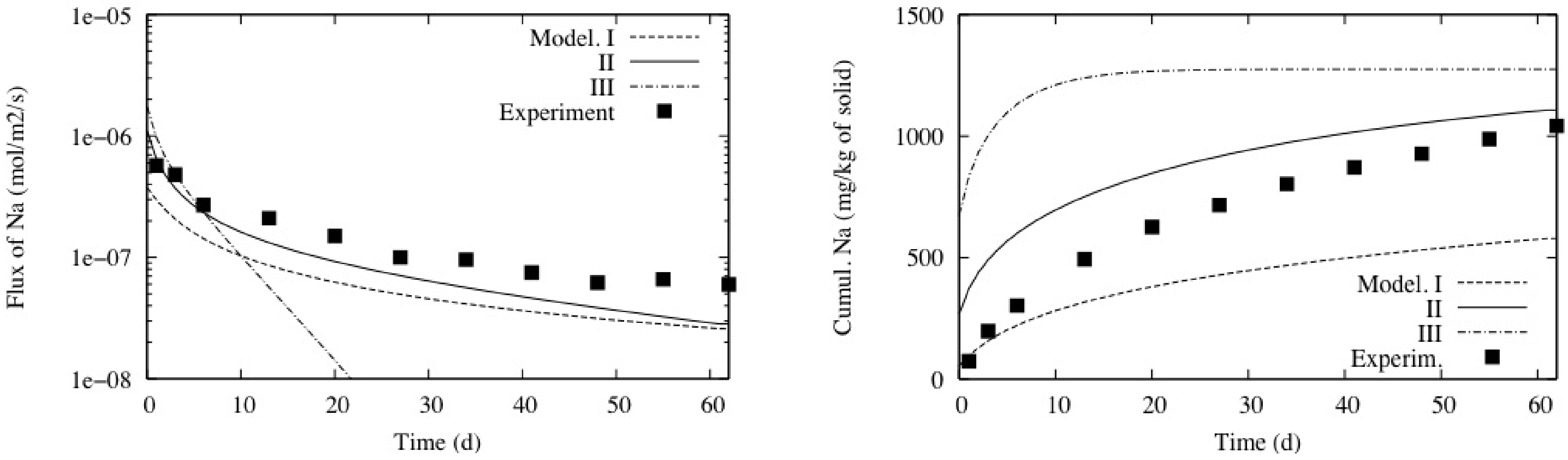
Stage 2



➢ Needs for a “common” modelling approach and code applied to different scales, as mechanistic as possible

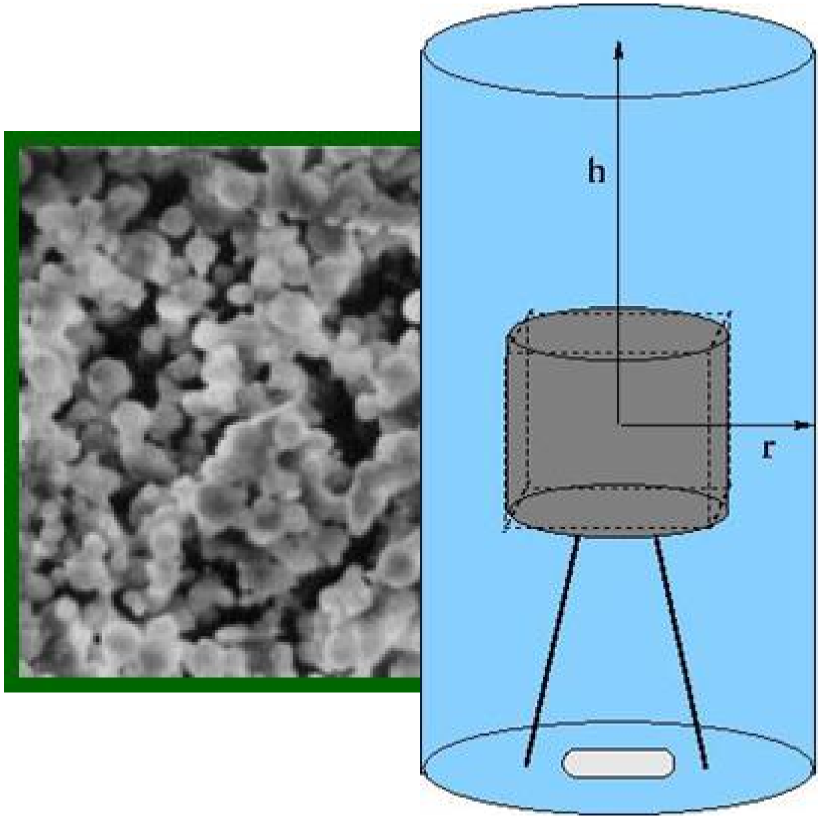
- Reactive transport codes are good candidates

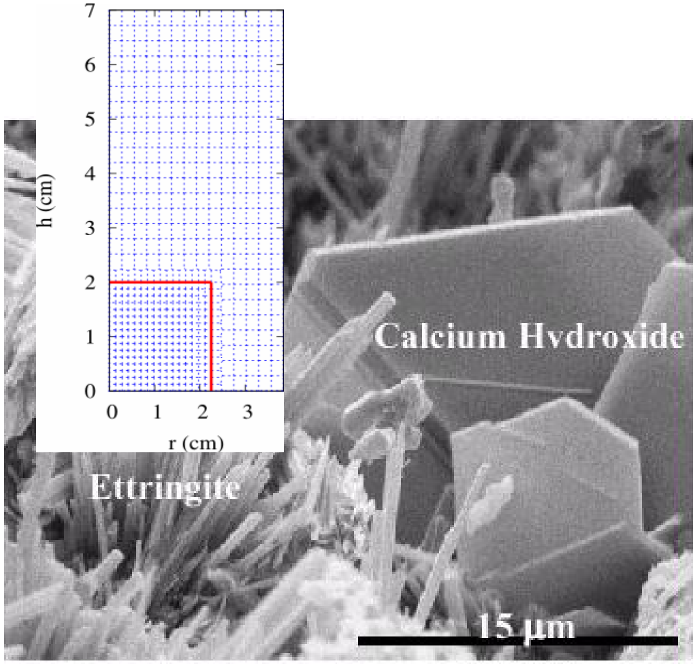
Sodium release during dynamic leaching



- conservative diffusion-controlled assumption globally applicable
- > 99% of the initial total inventory is leached for 250 ml/h
- (+ slight effect of the renewal leachant rate)

What's the surface of a porous media



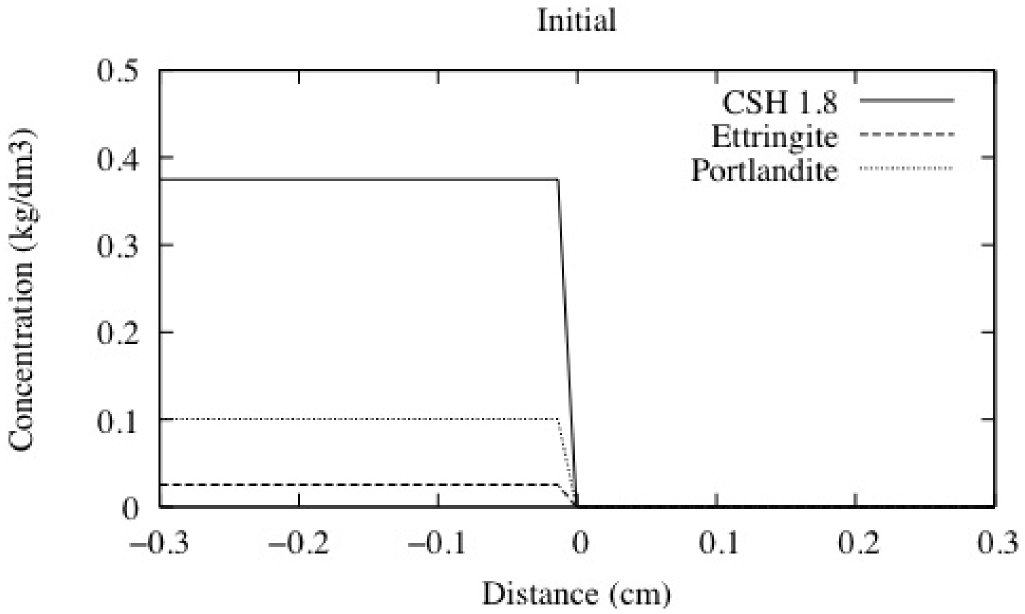


⇒ Elementary Volume Representation of the interface rather than a geometrical surface

⇒ Equilibrium approach, diffusion-controlled (in a first step)

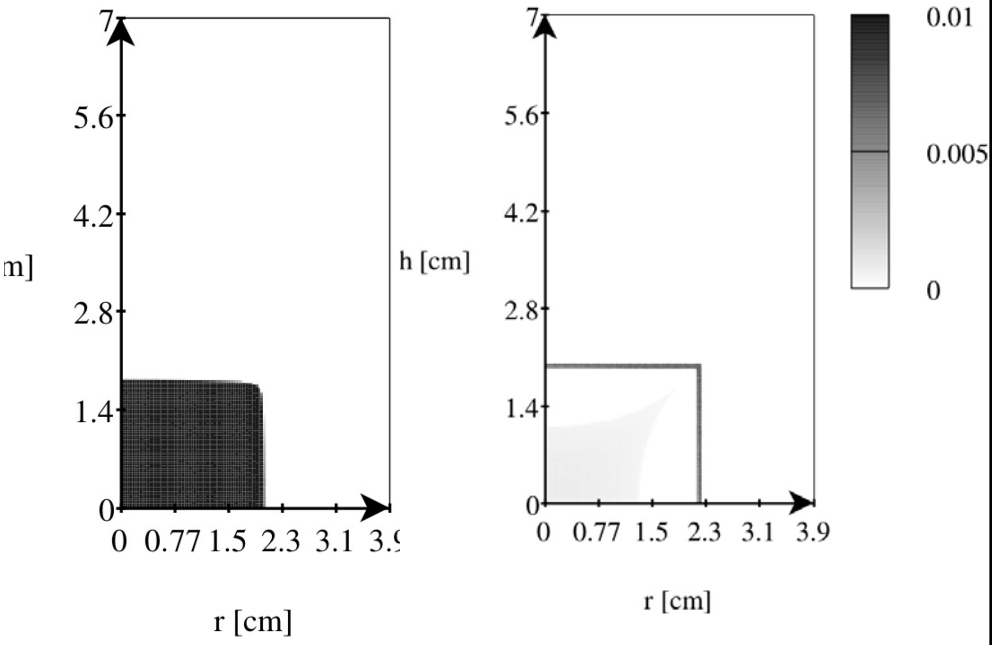
Mineralogical evolution

(A-A’, edge)



Two main distinct main fronts

(slightly) speeded up by porosity opening



AFm dissolution and hydrotalcite precipitation

Element release *vs* grid refinement

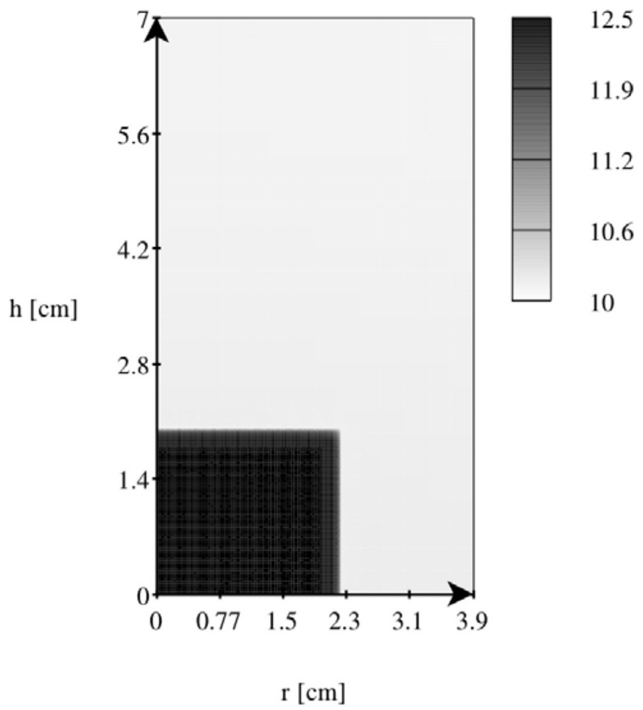
Sensitivity of the calculated cumulative releases (mg/kg of solid) with respect to the refinement of the calculation grid.

Node size (m)	Na	K	Ca	Pb	H_4SiO_4	Cl	SO_4
2.5×10^{-3}	1 100	285	1 290	11	4.5	670	80
1.25×10^{-3}	1 100	285	2 750	35	6	760	80
6.25×10^{-4}	1 100	285	4 585	54	13.5	760	96
3.1×10^{-4}	1 100	285	5 000	63	58	715	125
1.5×10^{-4}	1 100	285	5 000	67	250	715	150
1.5×10^{-4} (*)	1 100	285	9 200	132	2 050	715	240
Experimental	1 050	350	15 840	70	12 750	500	245

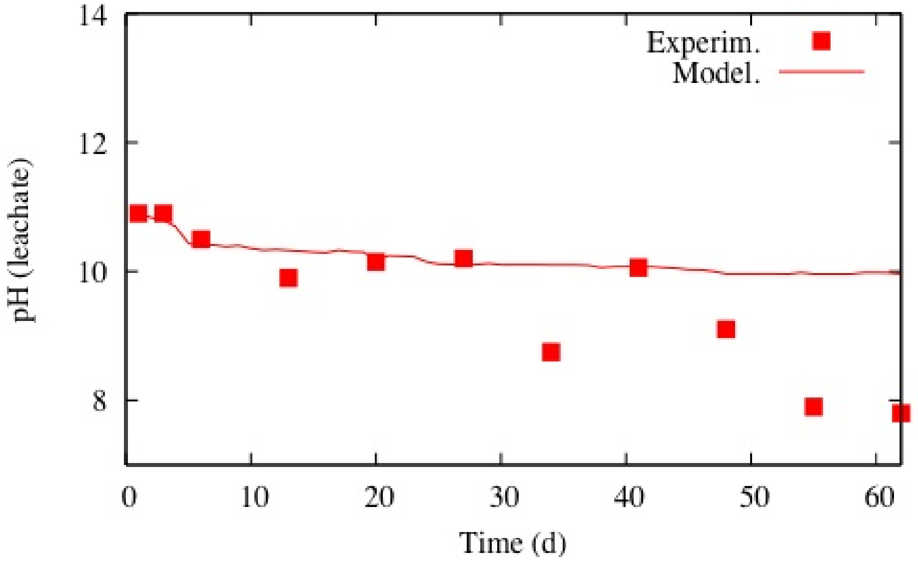
(*) This simulation takes into account the feedback of mineralogical evolution on porosity and diffusion coefficient.

pH evolution during dynamic leaching

in the monolith

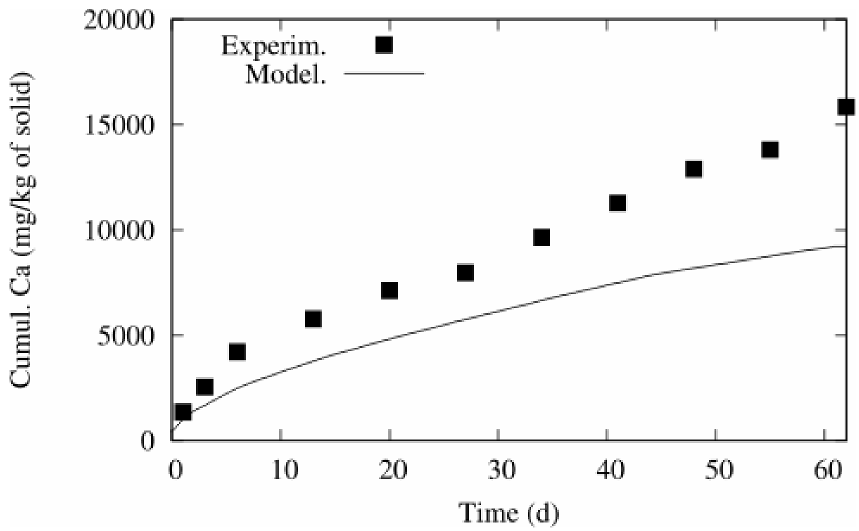


in the reactor vessel

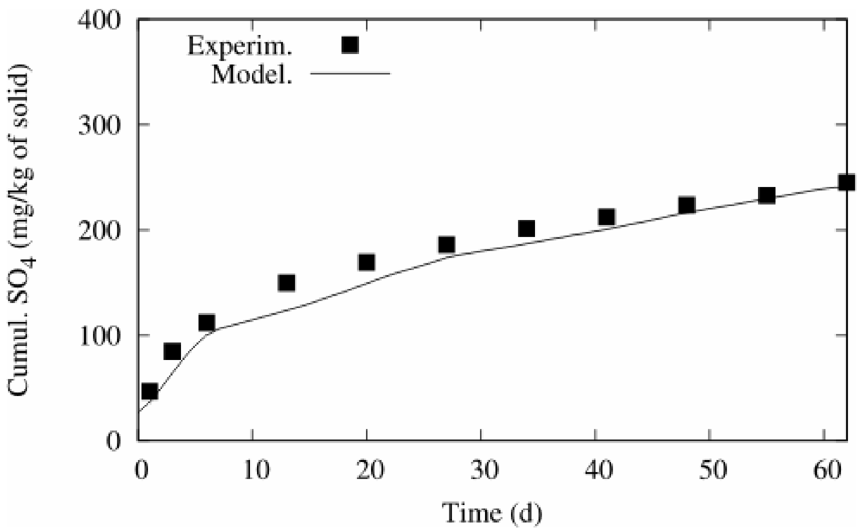


- pH profiles can be calculated in the monolith itself (function of Na-K diffusion and portlandite dissolution)

Calcium and sulfate releases during dynamic leaching



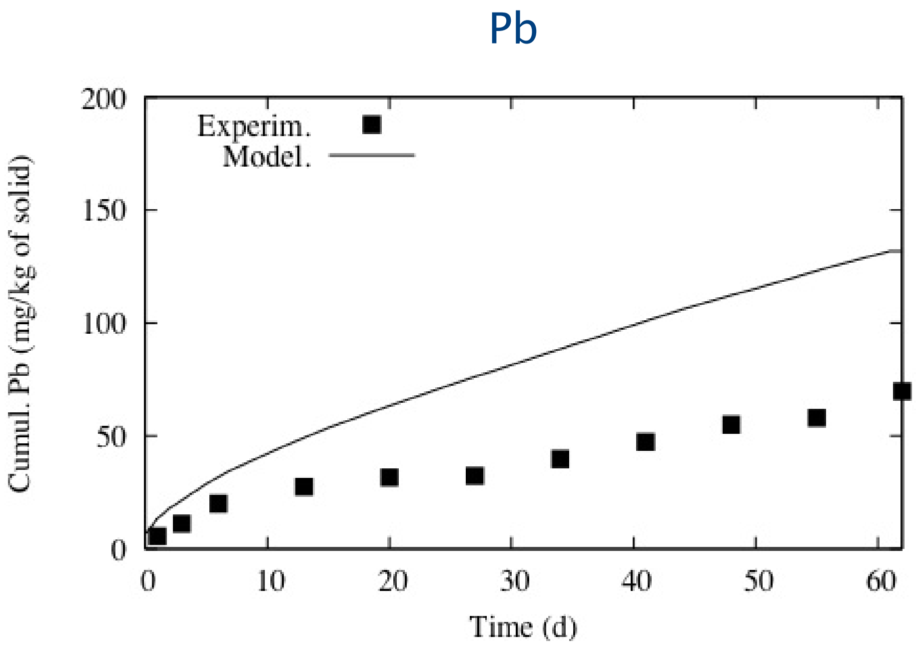
Ca



SO_4

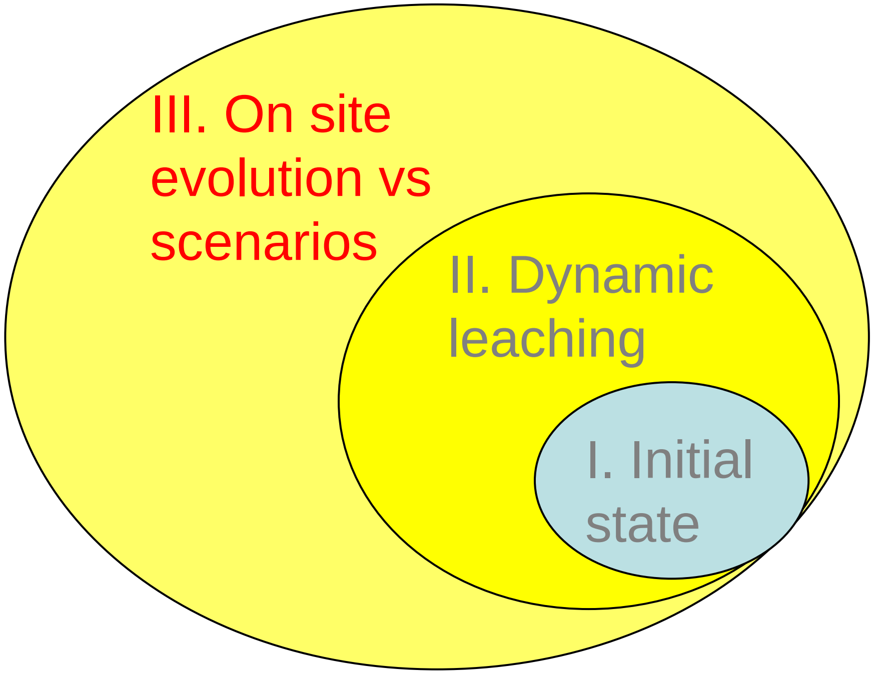
- Essentially solubility-controlled (monolith "surface" dissolution)
- Initial total inventory almost unchanged for Ca

Lead release during dynamic leaching



- Diffusion and solubility controlled
- Less than 0.5% of the initial inventory is leached for 250 ml/h

Stage 3



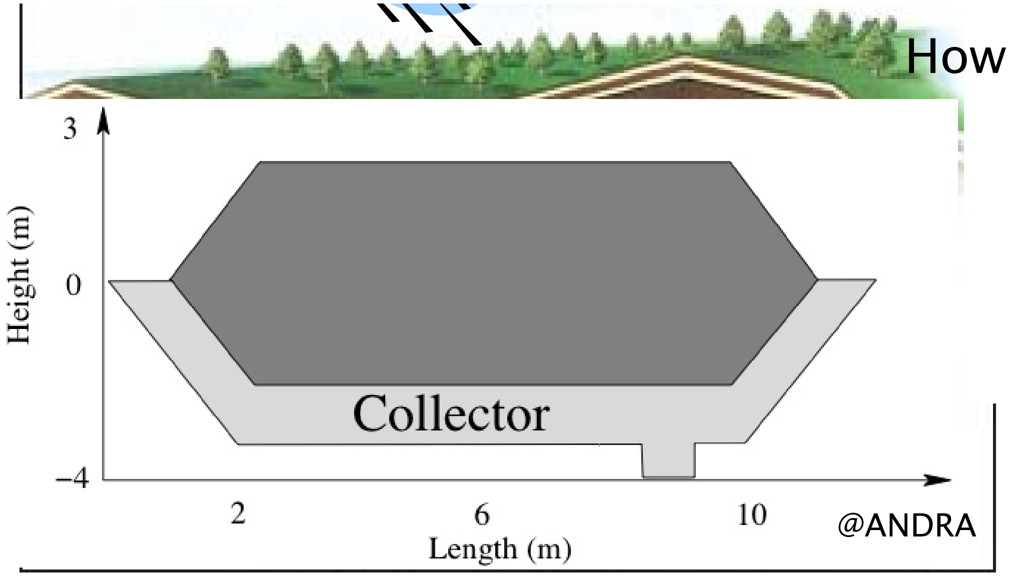
- ➢ Needs for a “common” modelling approach and code applied to different scales, as mechanistic as possible
  - ▪ Reactive transport codes are good candidates

Cementitious waste disposal scenarios

Effective infiltration

ermal stress, ageing (, water radiolysis) might induce micro to macro cracks.

How this would impact on toxic waste release?



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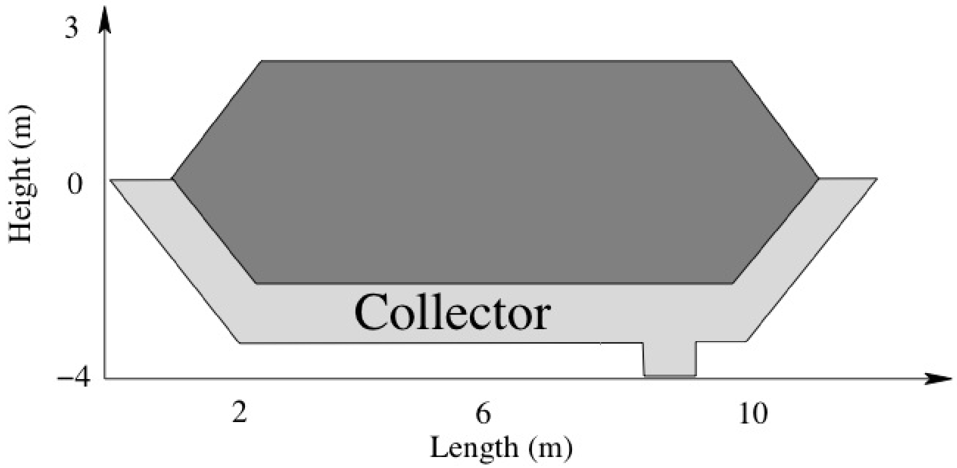
- Test–case A = undamaged monolith (~1 m^3)
- Test–case B = macro–fractures
- Test–case C = micro–crack network

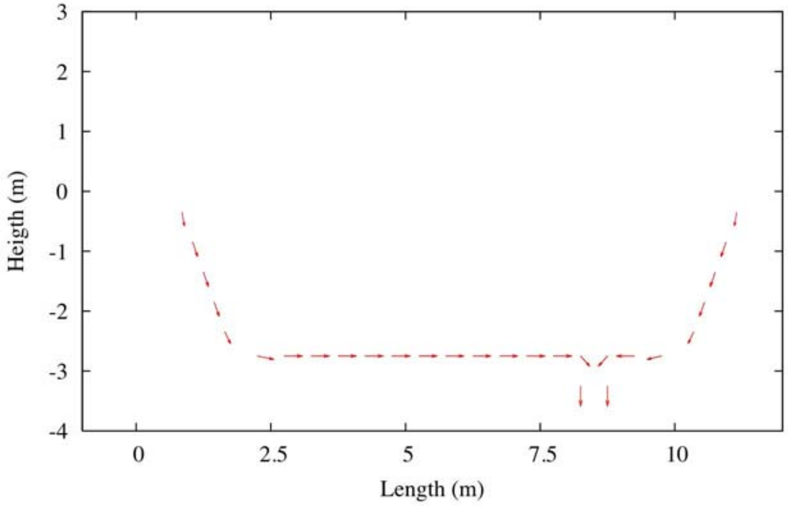
$$\frac{\partial \omega c_i}{\partial t} = \nabla \cdot (D_d \nabla c_i - c_i U) - \frac{\partial \omega \bar{c}_i}{\partial t}$$

+ dual porosity

Disposal scenario with undamaged waste

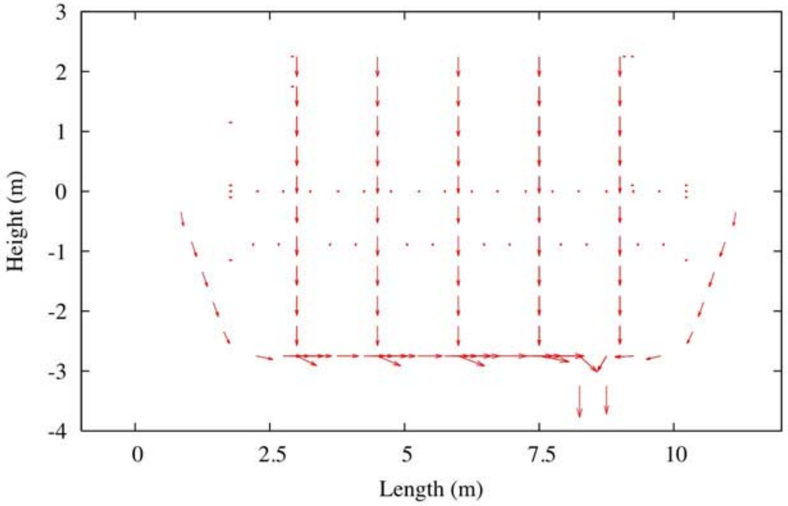


Test-case A = undamaged monolith

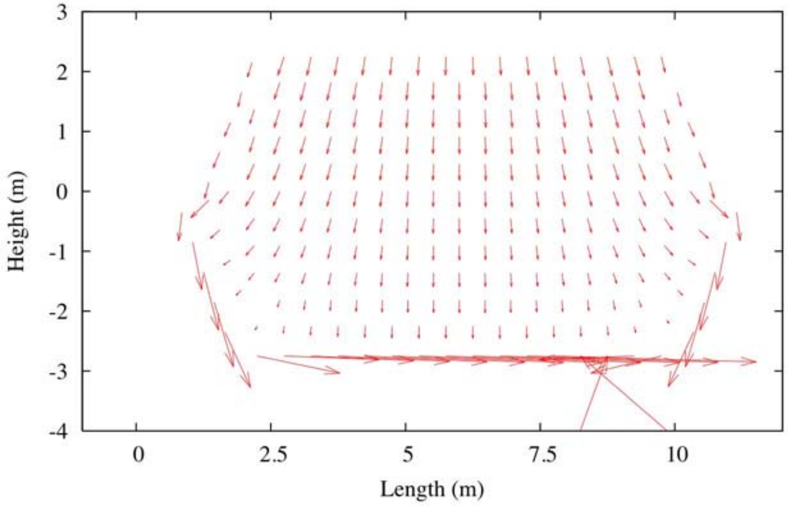


Disposal scenario with fractures or cracks

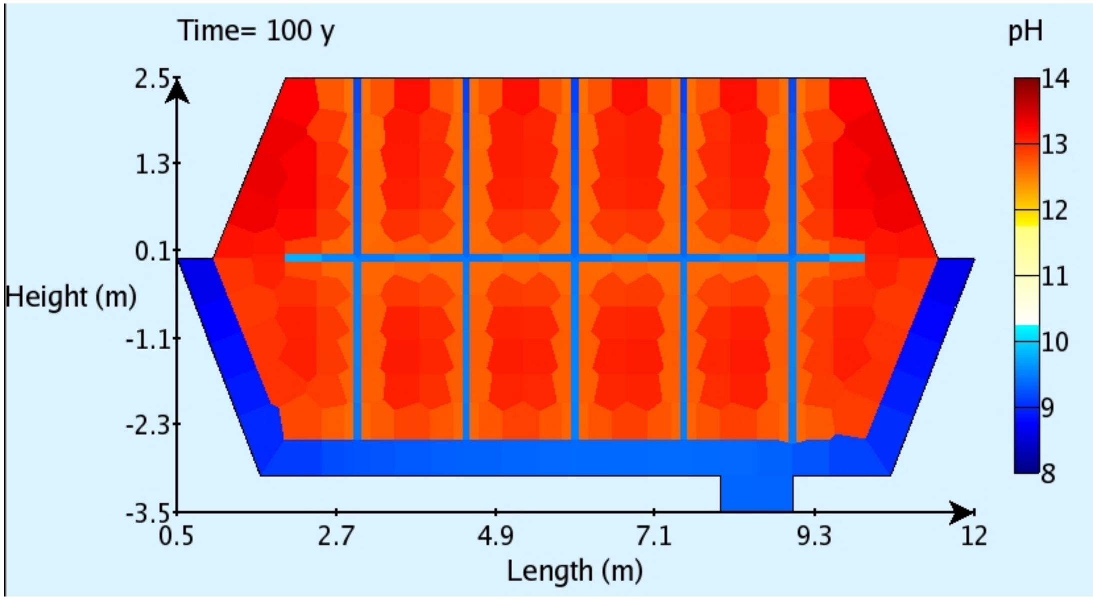
Test-case B = macro-fractures



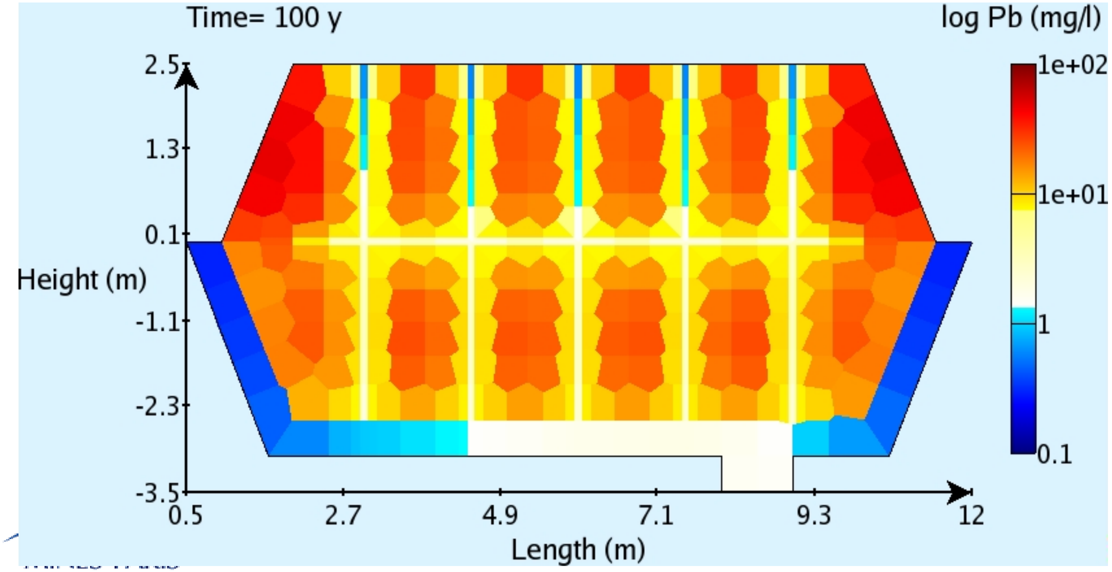
Test-case C = micro-crack network



Evolution of pH and lead aqueous conc. (case B)

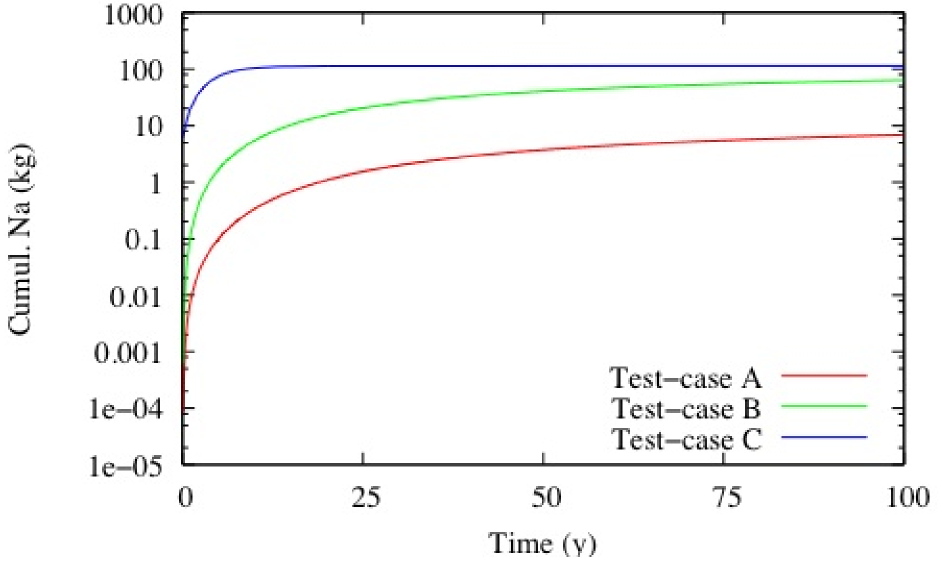


- Diffusion of alkaline (monolith → fractures) followed by slow advection
- Portlandite buffering vs CO_2 reactivity (→ calcite precipitation)

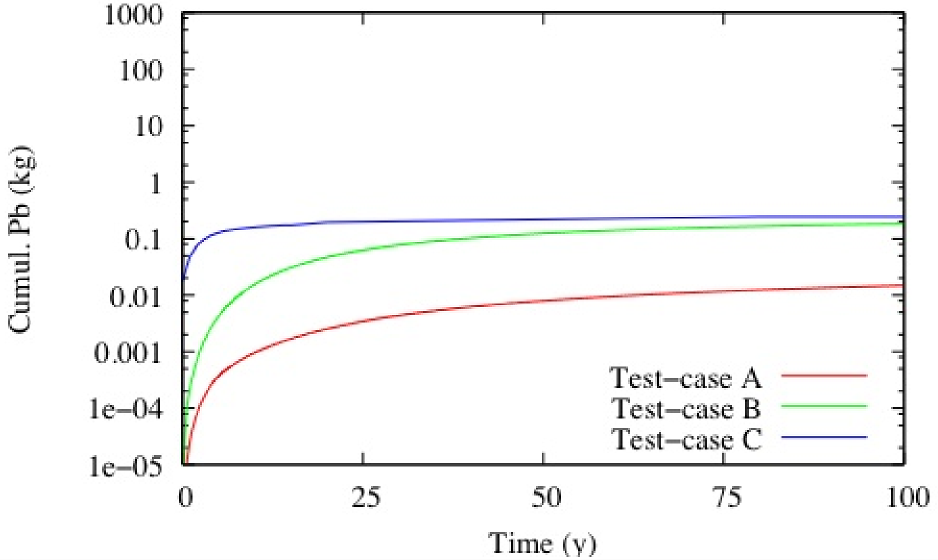


- Same diffusion-convection scheme
- Coupled to pH changes
- Pb may co-precipitate with calcite

Sodium and lead cumulative releases (100 y)



- Tracer, therefore relevant to assess the effect of hydrodynamic regime on release
- → clear contrasted behaviors



- Sensitive to both hydrodynamics and pH evolution
- However, the released lead fraction << dynamics leaching test ones

Concluding remarks (I)

- Modeling the initial state required preliminary mineralogical analyses and batch leaching tests.

- This core source term model → dynamic leaching 3D-simulations considering, simultaneously, pore water evolution, mineralogical alteration fronts, and the concomitant release of elements → *efficient Pb containment.*

- However, process-oriented modeling is time consuming and the S/S waste evolution was not fully addressed due to the complexity of cement-based materials (especially for pollutants) and lack of (sorption) data.

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Concluding remarks (II)

- Capability of reactive transport codes to extrapolate the laboratory results to site scenarios, illustrated here by an hypothetical but demonstrative effect of cracking processes on long-term pollutant releases in disposals.

- Capability of reactive transport codes to support performance and environmental impact assessments.

- Major perspectives = i) unsaturated (two-phases) modeling, especially for carbonation effect, ii) sorption data and iii) redox state(s).

Contact and further information

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De Windt, L., Badreddine, R. (2006). Modelling of long-term dynamic leaching tests applied to solidified/stabilized waste, *Waste Management, in press*, doi:10.1016/j.wasman_2006.07.019.

De Windt, L., Badreddine, R., Lagneau, V. Long-term reactive transport modelling of stabilized/solidified waste: from dynamic leaching tests to disposal scenarios (2006), *J. Hazard. Mater. ,in press*, doi:10.1016/j.hazmat.2006.03.045.

Thank you for your attention !

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