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WELL MATERIALS AGEING IN A CONTEXT OF H_2S-CO_2 GEOLOGICAL STORAGE

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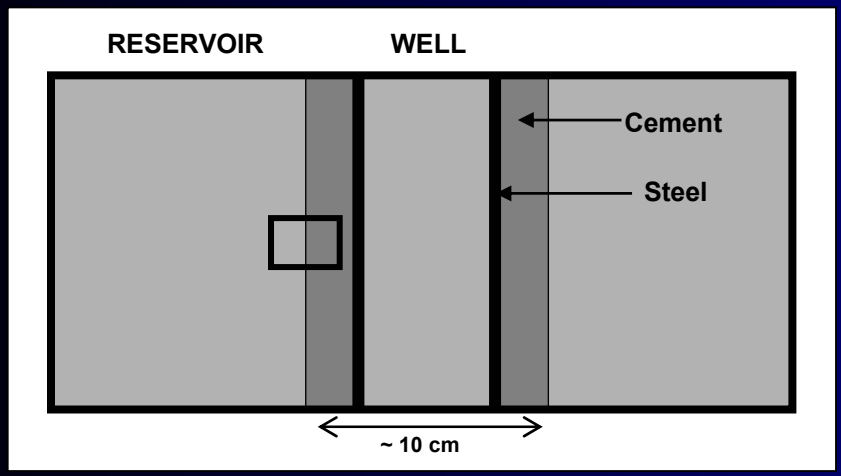
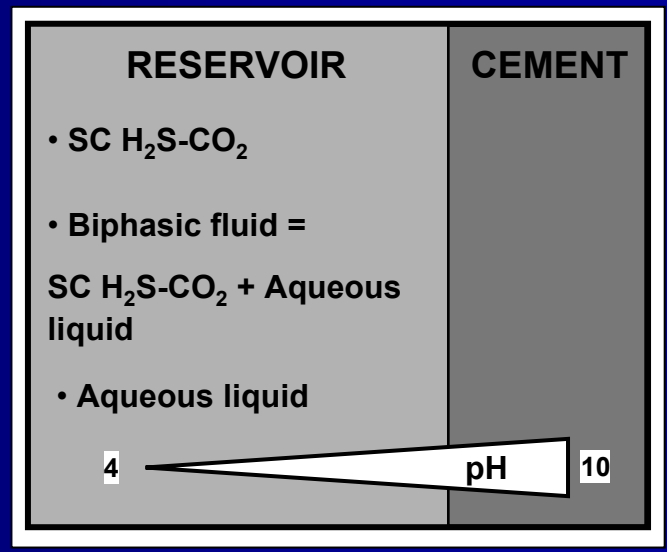
One issue: the leakage through deteriorated wells





- Different cement-fluids contacts
- High P-T conditions

→ Alteration of the materials

→ Pathway for leakage to the surface

SCOPE OF THE STUDY:
Evaluation of the well materials durability in such environment

Plan

1 - EXPERIMENTAL AND ANALYSIS PROTOCOL

2 - STARTING MATERIALS

3 - EXPERIMENTAL APPROACH

4 - NUMERICAL APPROACH

1-Experimental and analysis protocol

1. Experimental protocol
2. Analysis protocol

Experimental apparatus

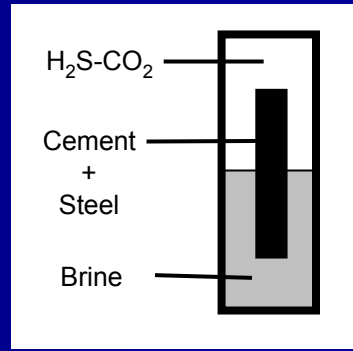
AUTOCLAVES AND REACTORS

- Systems at geological relevant P-T

→ Hydraulic pressure autoclaves (Max. cond.: 1000 bar-450°C)

- Systems with high concentration of gas – Safety rules

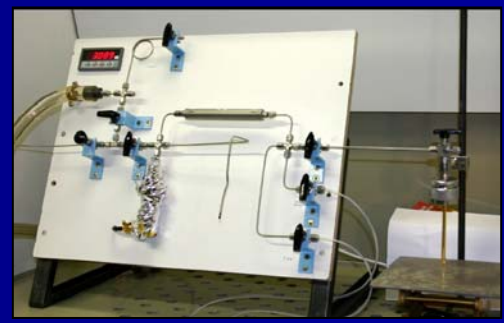
→ Use of micro-reactors (gold capsules of 2 cc)



GAS LOADING IN THE CAPSULES

- Specific apparatus under the form of a gas line

→ Allows to introduce safely a precise mass of gas in the capsules



1-Experimental and analysis protocol

1. Experimental protocol
2. Analysis protocol

Analysis of cement and steel

1. STEEL

- Optical microscopy
- SEM
- TEM

2. CEMENT

- X rays diffraction
- SEM → elemental mapping
- Raman micro-spectroscopy → mineralogical mapping
- TEM
- Water porosimetry

Analysis of the fluids

1. **Recovery and quantitative analysis of the residual gas using the gas line**

   --> Mass balance of the gaseous species --> amount of mineralized gas

2. **Synthetic fluid inclusions**

   --> *in situ* sampling of fluids surrounding the materials

   --> visualisation of the number and state of fluid phases

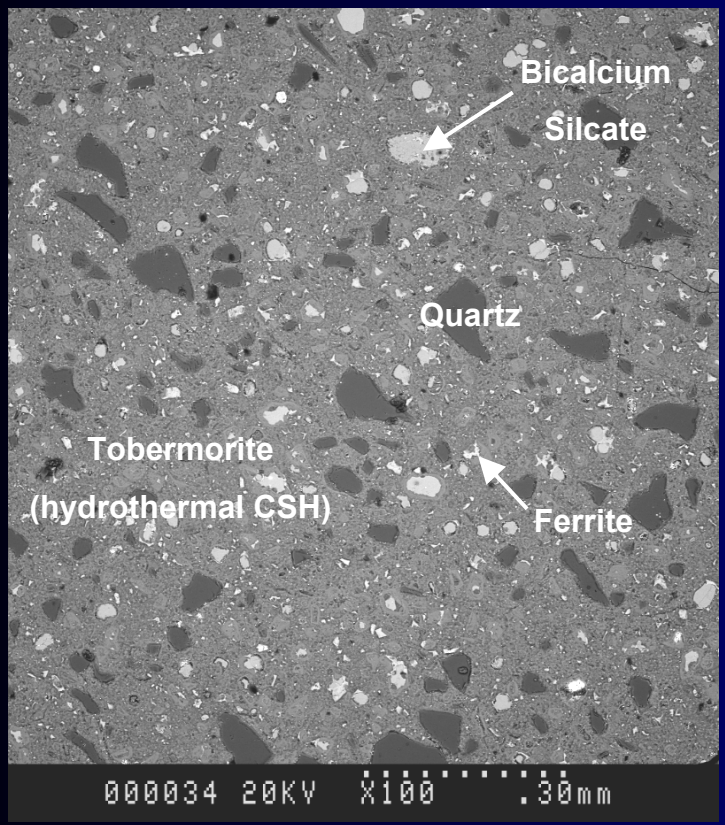
   --> Composition of the phases (speciation of liquid, concentration, …)

2-Starting materials

The starting materials: analogues of deep well materials

CEMENT (slurry hardening)

- The slurry has a typical composition of deep well cement slurry
- It hardened in hydrothermal conditions during the cure



• Assemblage of Tobermorite + Quartz

STEEL:

• used for the casing

• low C content

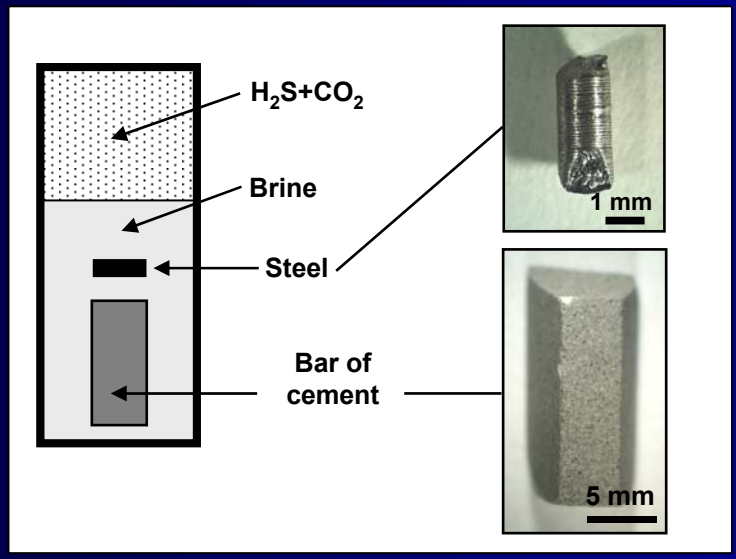
--> Fe° (98 mol%)

3-Experimental approach

1. Experimental conditions
2. Results

Geologically relevant conditions

Cement under the form of bar



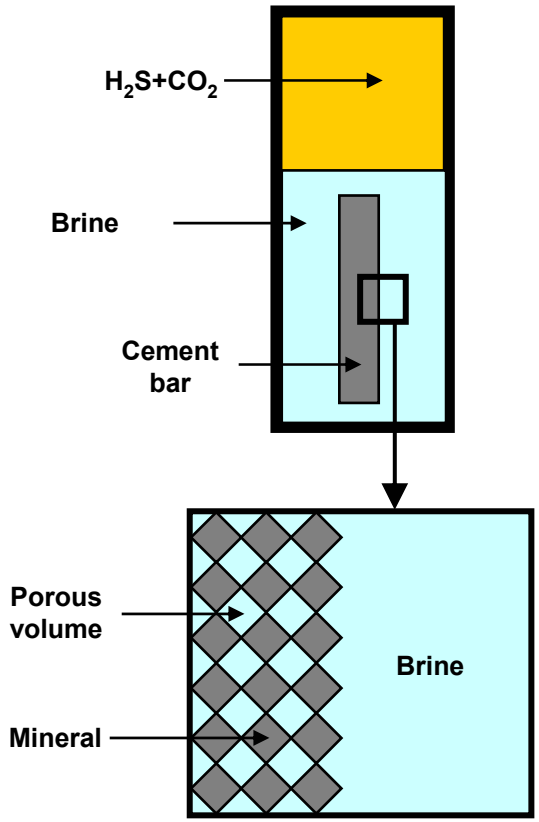
RESERVOIR ⟺ EXPERIMENTS

- **FORMATION WATER:** NaCl brine (150 g/l)
- **TOTAL PRESSURE:** 500 bar
- **TEMPERATURE:** 120°C, 200°C
- **GAS:** 66mol% H_2S + 34mol% CO_2

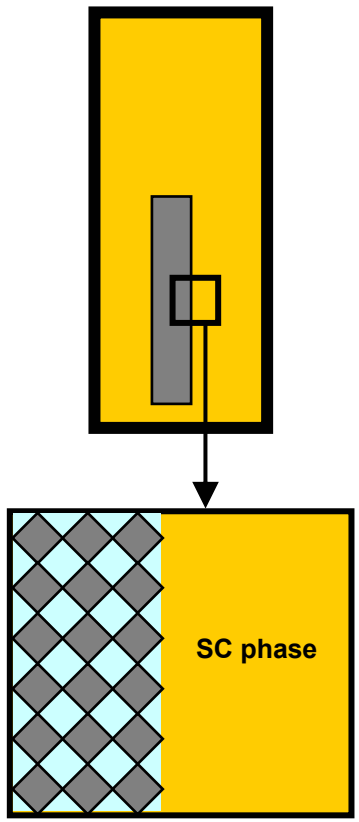
Three fluids at the cement-external media interface

3 types of ageing exposures

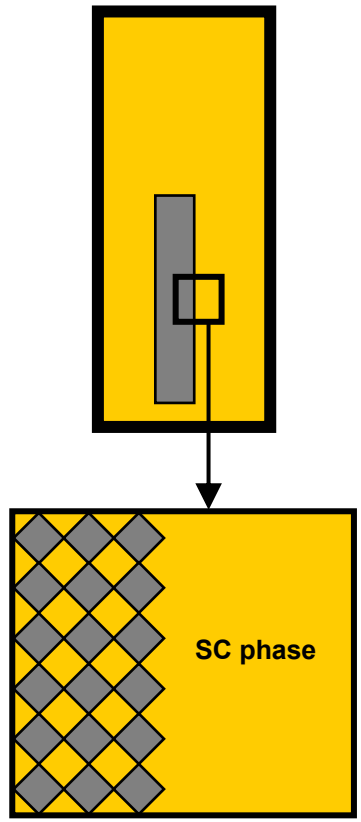
LIQUID (L)



BIPHASIC (L+S)



DRY SC (S)

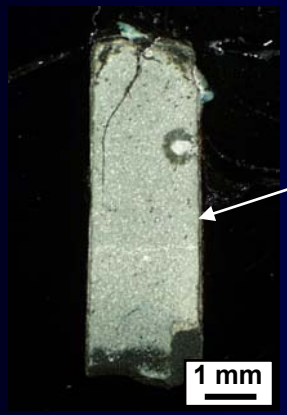


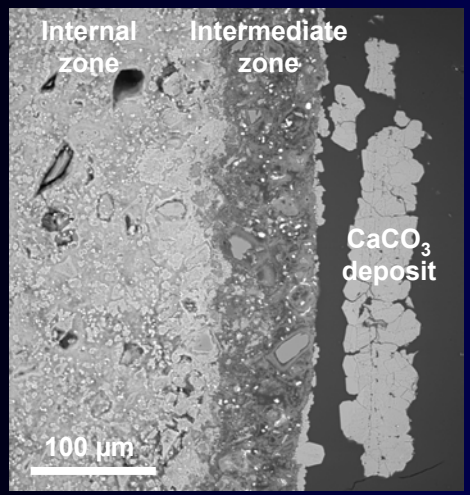
3-Experimental approach

1. Experimental conditions
2. Results

Different carbonation profiles according to the exposures

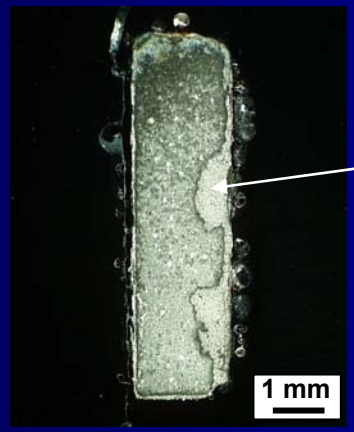
L

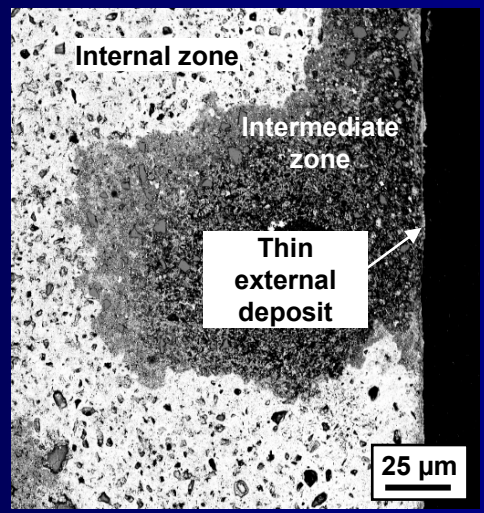




- Constant thickness front
- Massive deposit of $CaCO_3$

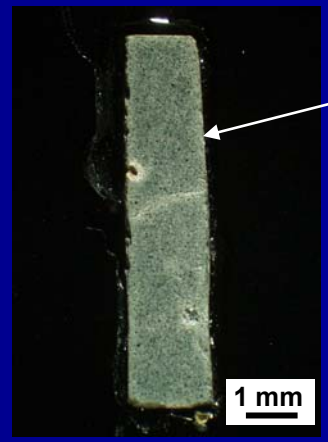
L+S

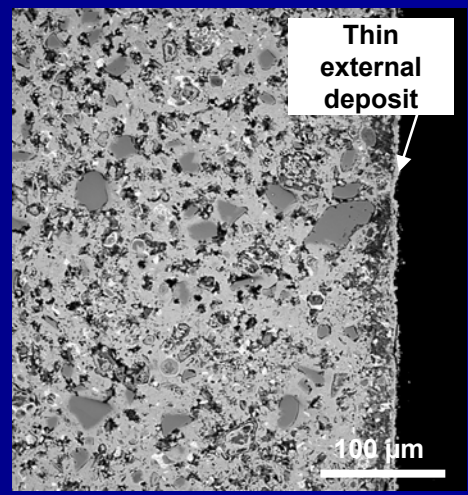




Variable thickness front

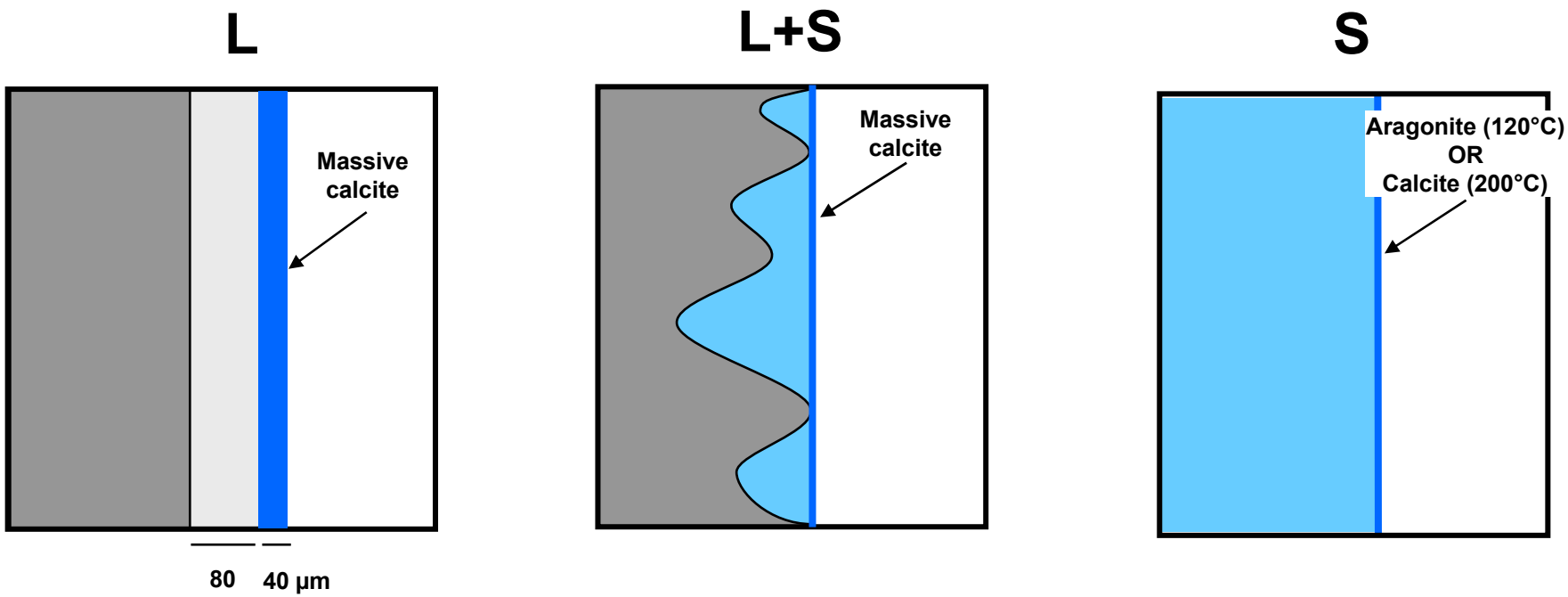
S





Total homogeneous alteration

Schematization of the carbonation profiles



"NO ALTERED" CEMENT | DECALCIFIED CEMENT | CARBONATED CEMENT

Diffusion of C and Ca species
→ Massive deposit of calcite
→ Diffusive blockage
→ Alteration stopping

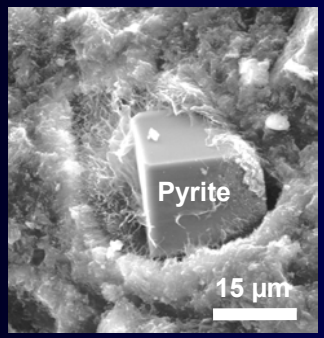
Intrusion of the SC into the porous volume
→ digitations

Total carbonation (favorised by the absence of liquid water and optimal diffusion of the SC CO_2)

The sulfidation of the iron bearing phases

1. IN THE CIMENT: THE SULFIDATION OF THE FERRITES

200°C

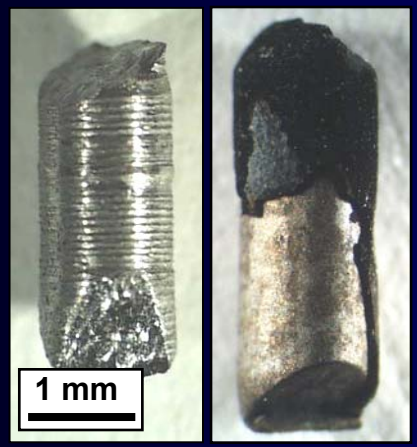


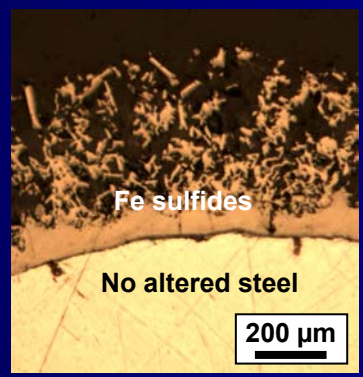
$$Ca_2AlFeO_5 + 2\,H_2S \rightarrow FeS_2 + \ldots$$

2. THE SULFIDATION OF THE STEEL

$$Fe° + H_2S \rightarrow FeS + H_2$$

Before After



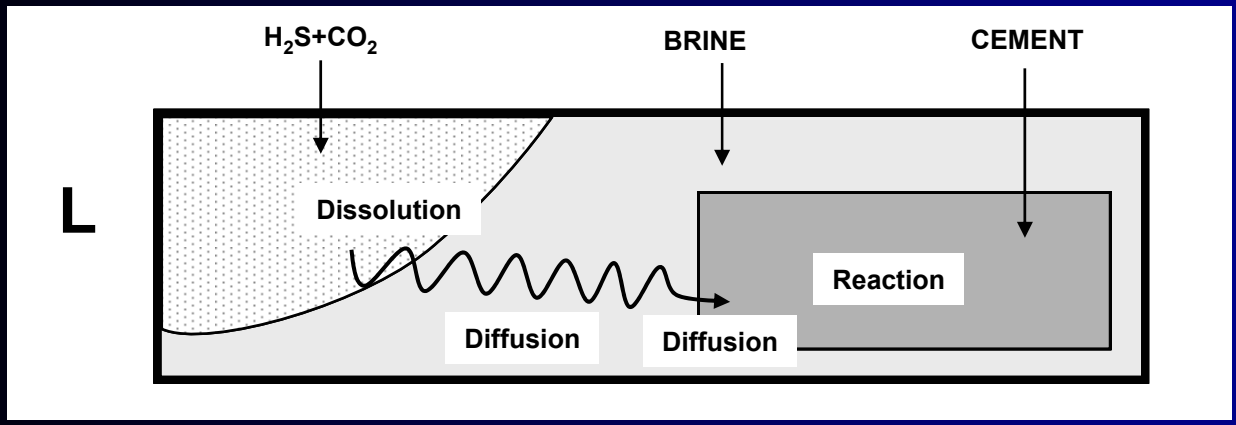


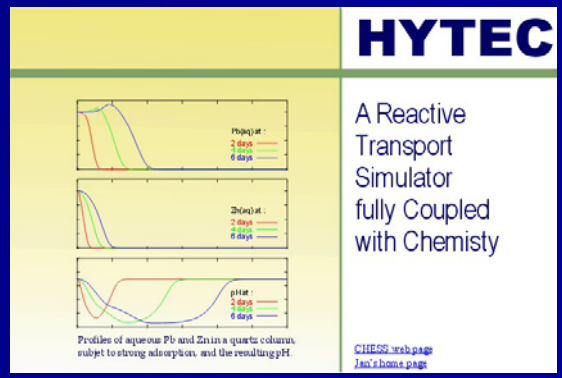
Iron sulphide crust

Group of pyrrhotites

4 – Numerical approach

Cement alteration: a result of coupled processes

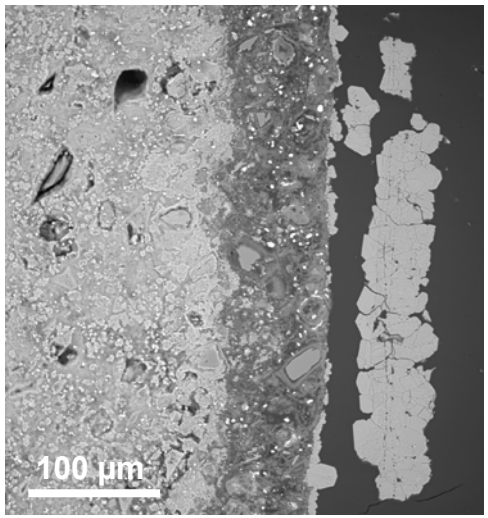


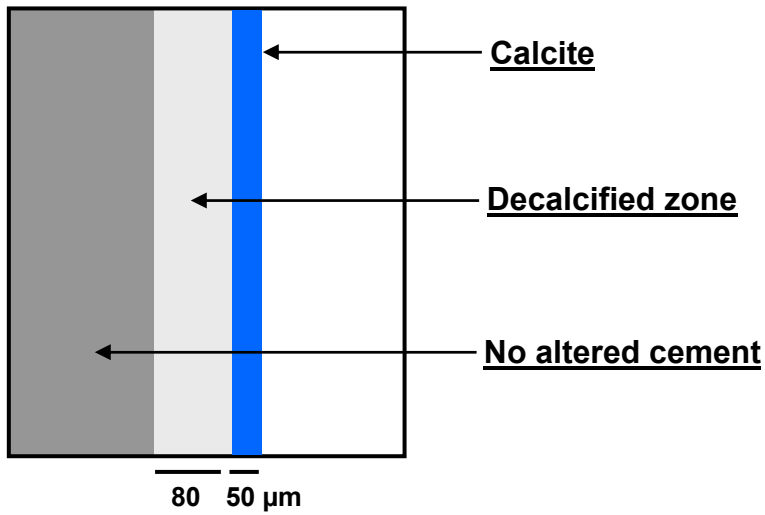


→ Need of a coupled chemistry-transport code (HYTEC)

SCOPE: Reproduction of the experimental results by numerical simulation

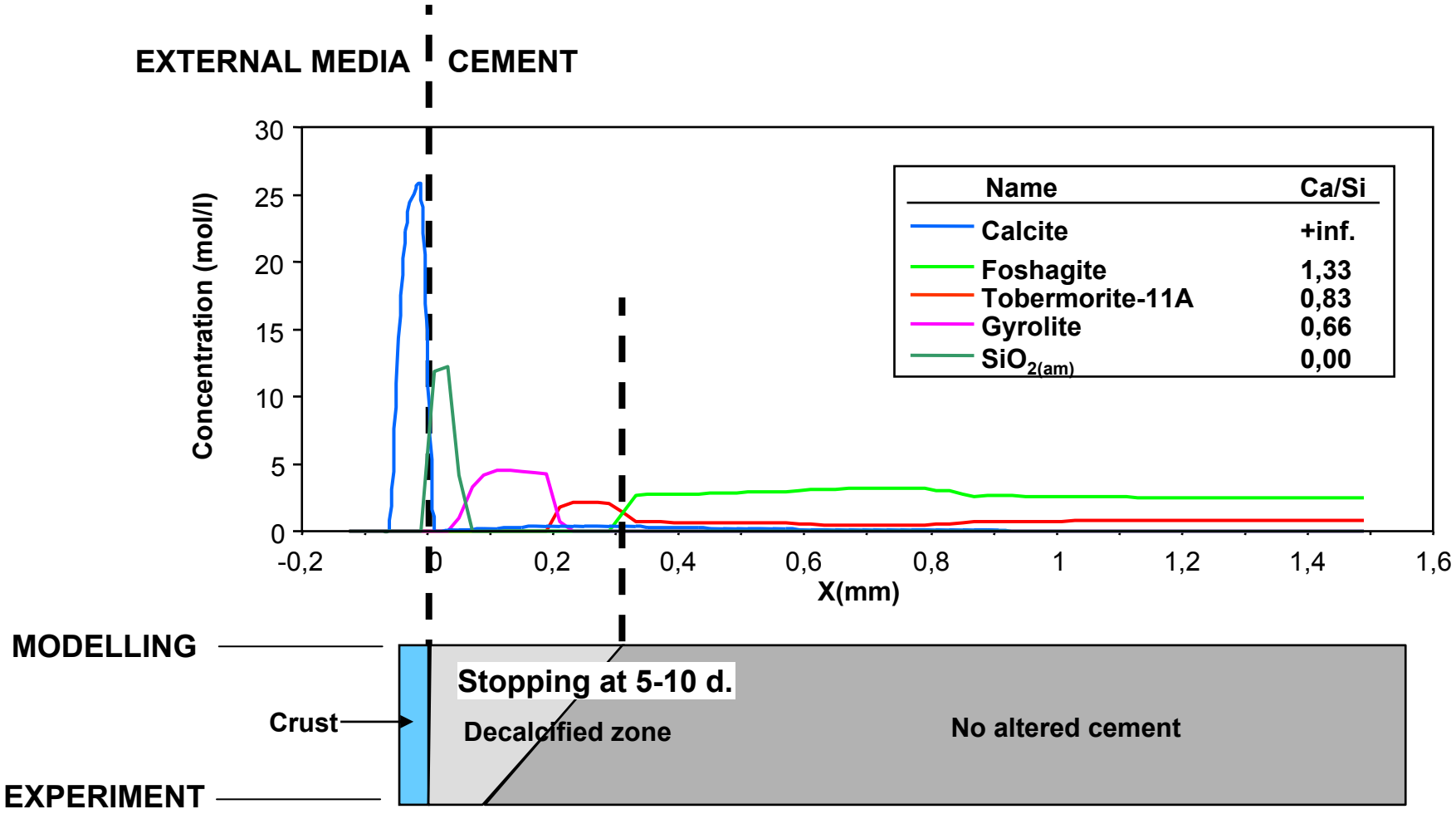
L
200°C





STOPPING OF ALTERATION BY DIFFUSIVE BLOCKAGE

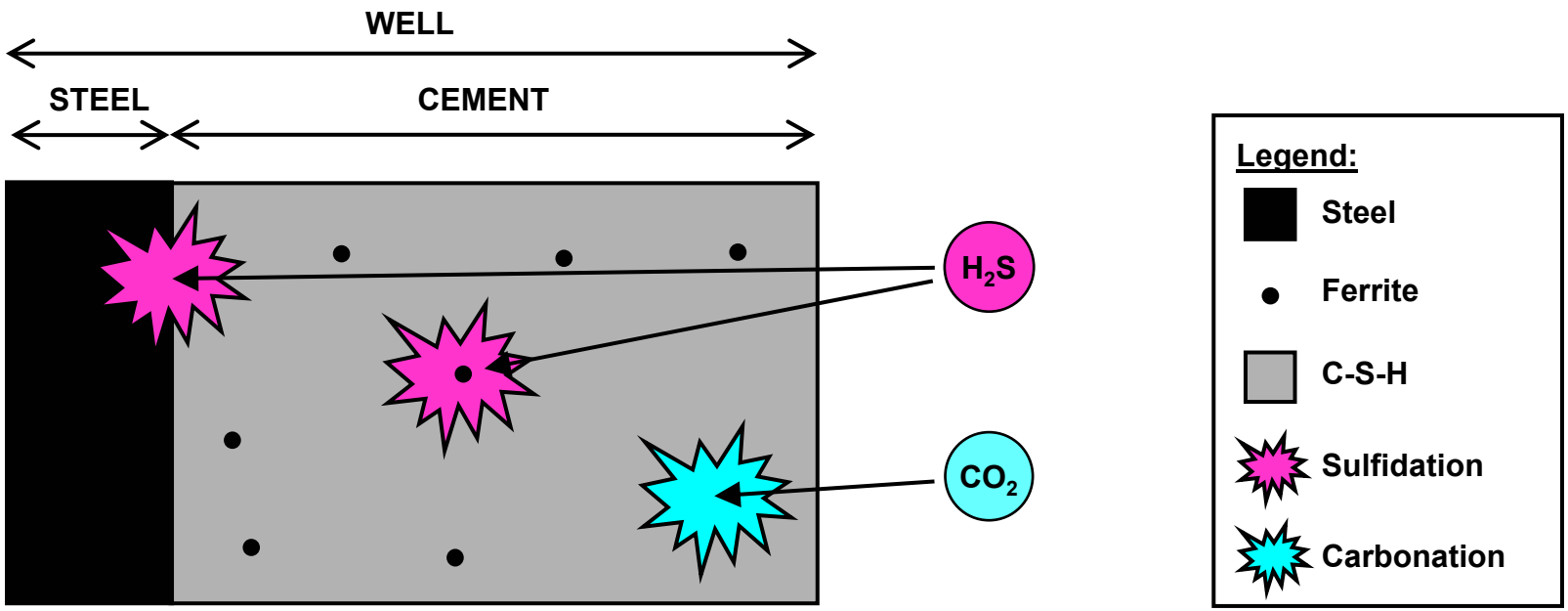
Modelling results



- Confirm the calcite deposit as the responsible of the stopping of the alteration that we observed experimentally
- Refine the model to fit the experimental and numerical front thicknesses

Conclusion

Distinctive reactions according to the material



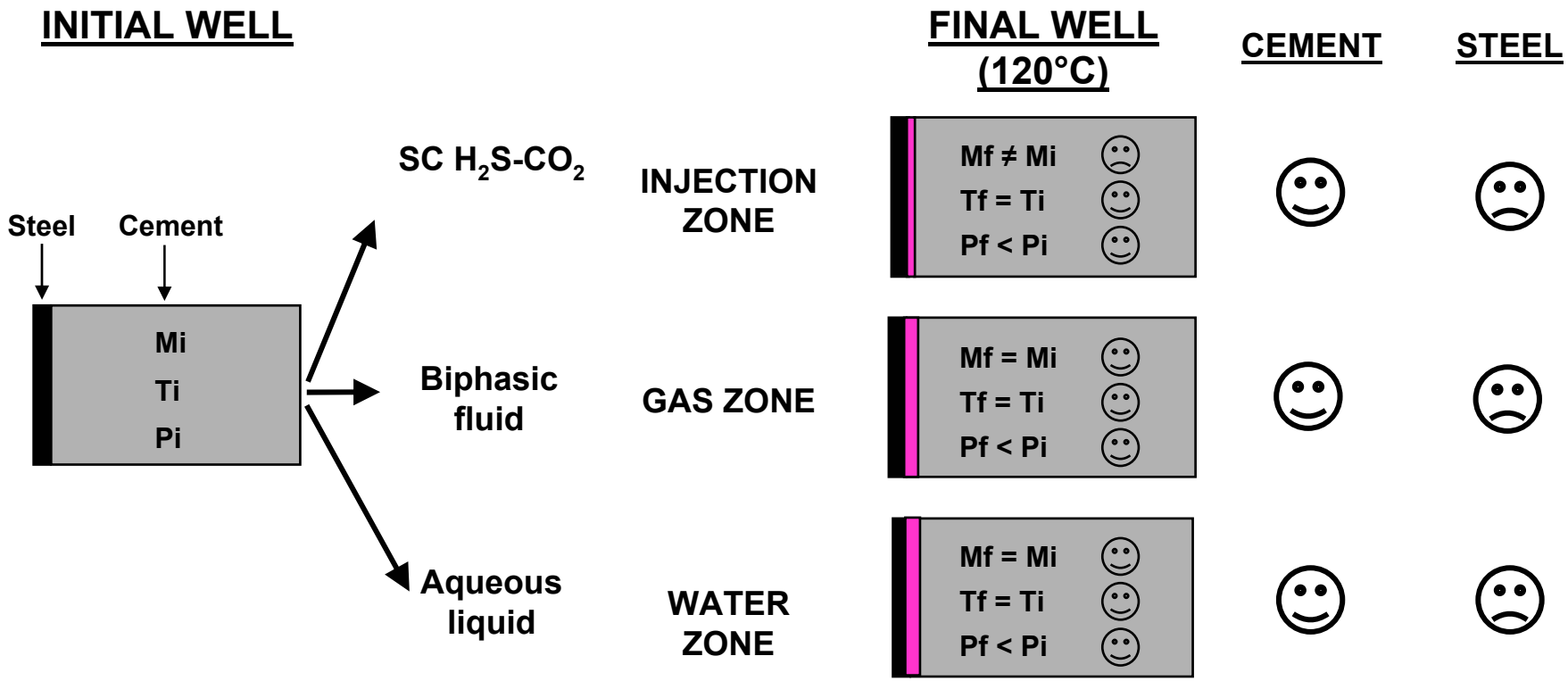
- The cement highly reacts with the CO_2 weakly with the H_2S
- The steel strongly reacts with the H_2S weakly with the CO_2
- 1st order parameter which controls the intensity degree of carbonation = fluid phase at the contact of the minerals

→ carbonation favoured without liquid water, max. within dry SC

Evaluation of the well durability (petrograph point of vue)

THREE CRITERIONS OF DURABILITY OF THE CEMENT:

- Mineralogic evolution: Mf = Mi →
- Textural evolution: Tf = Ti →
- Porosity evolution : Pf < Pi or Pf = Pi →



Limits and perspectives

• Ageing at 200°C: experimental T° is superior to the cure T° of the cement --> superposition of two processes (re crystallisation and alteration)

→ Ageing T° ≤ curing T° of the cement

• At reservoir scale:
1) volumic predominance of the reservoir rock / well,
2) flowing.
→ the fluids which interact with the well are:
1) at equilibrium with the reservoir rock,
2) renewed.

→ Reactive percolation experiments where the fluid is pre-equilibrated with the reservoir rock

• Exhaustive study of durability

→ Must take in account the mechanical properties variations of the materials

• Large spatial and time scale view on the alteration of well

--> Extrapolate the numerical results

COMPLEMENTARY SLIDES

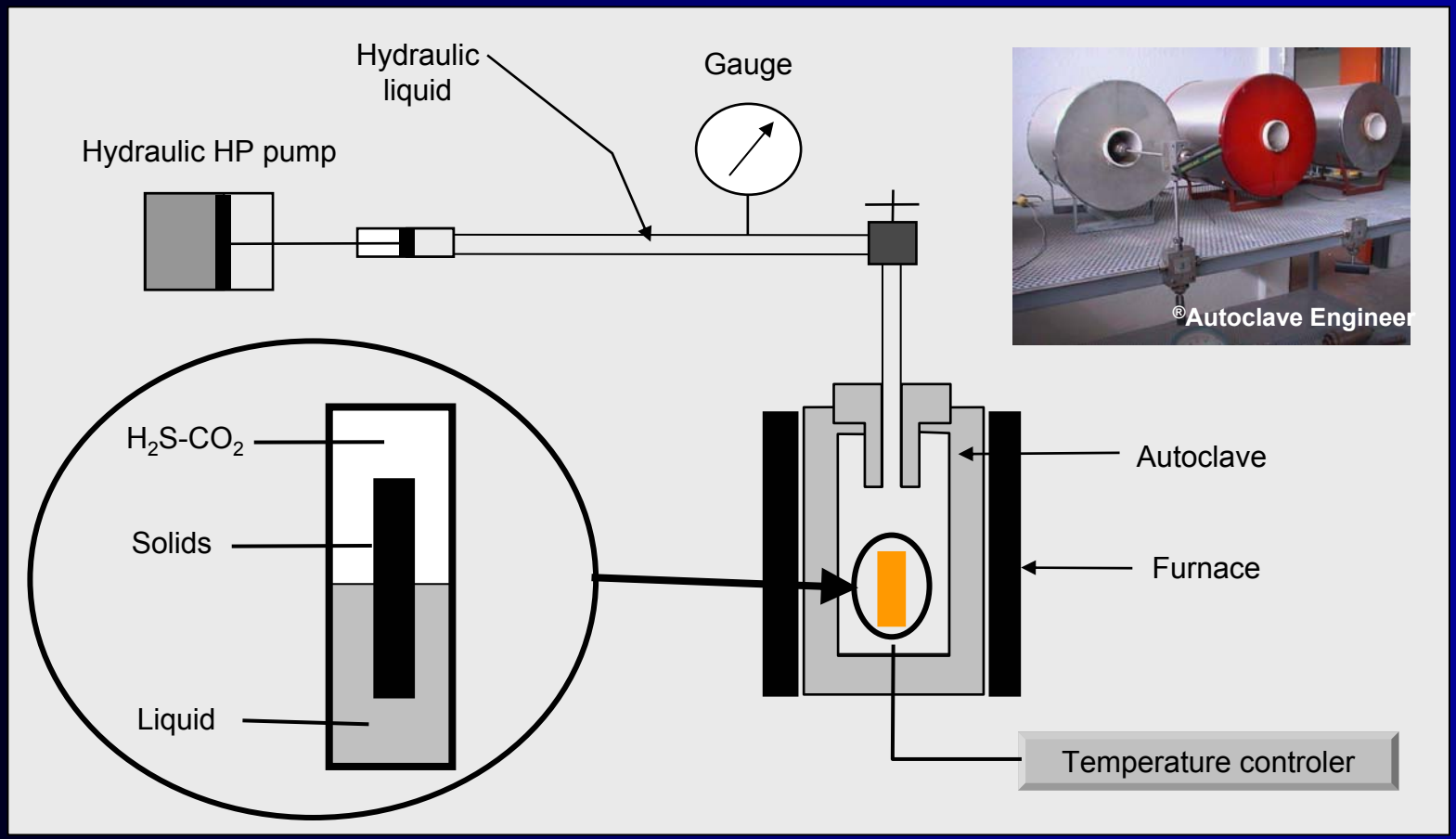
The micro-reactors and autoclaves

- Respect of geological relevant P-T

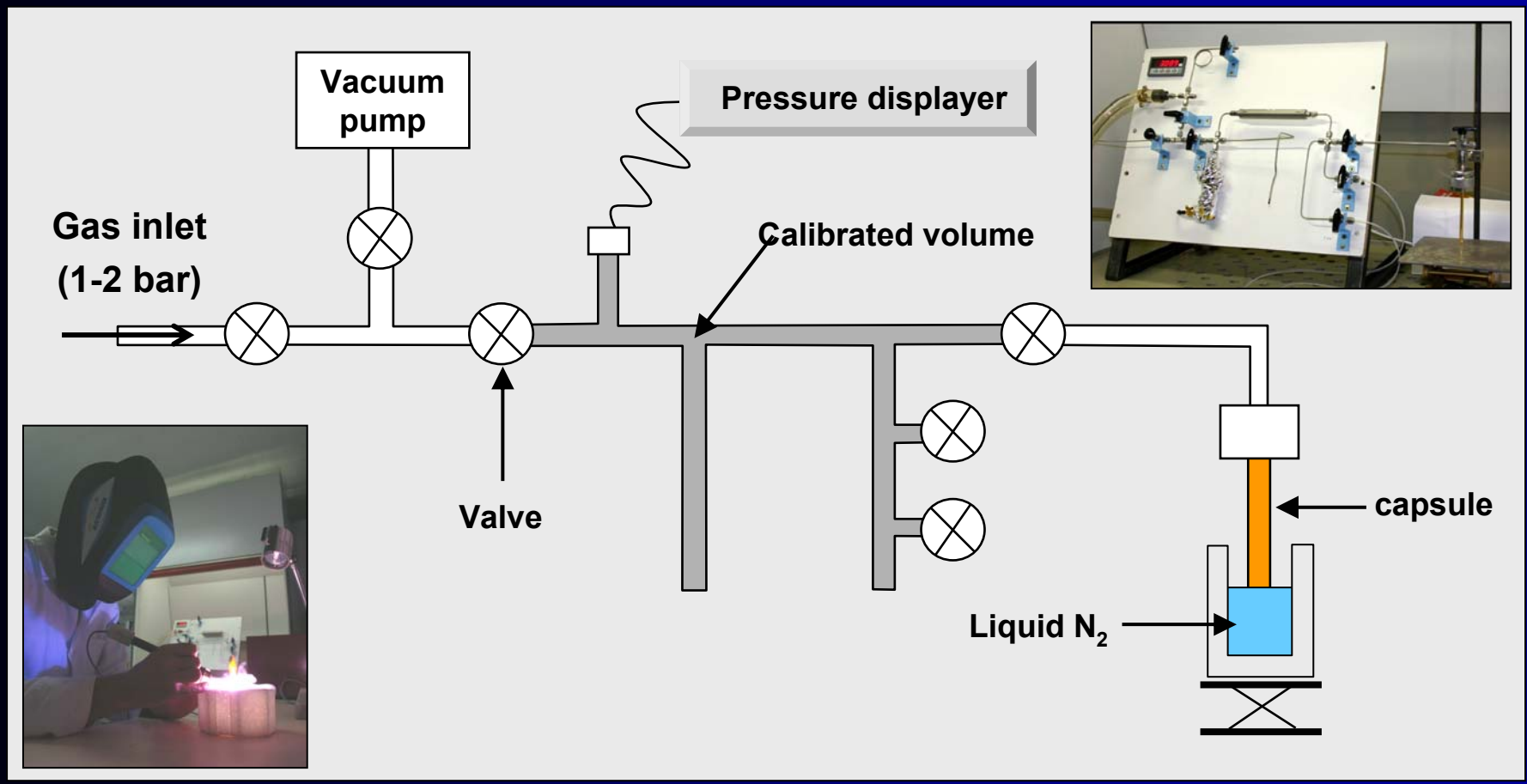
→ Hydraulic pressure autoclaves (Max. cond.: 1000 bar-450°C)

- Systems with high concentration of gas – Safety rules

→ Use of micro-reactors (gold capsules of 2 cc)



The secured gas loading in gold capsules



- Gas inlet and apparatus placed in hood in safe area
- The cryo-condensation allows a low pressure loading
- Precise mass of gas in the capsules

Terminology in cement chemistry and specific mineralogy

Oxide	CaO	SiO_2	H_2O	Al_2O_3	Fe_2O_3
Designation	C	S	H	A	F

Mineral name	Simplified formula	Mineralogic formula
Hydrothermal C-S-H		
Tobermorite	$C_5S_6H_5$	$Ca_5Si_6O_{16}(OH)_2 \cdot 4H_2O$
Xonotlite	C_6S_6H	$Ca_6Si_6O_{17}(OH)_2$
Other minerals		
Quartz	S	SiO_2
Bicalcium silicate	C_2S	Ca_2SiO_4
Ferrite	C_4AF	Ca_2AlFeO_5

The starting materials: analogues of deep well materials

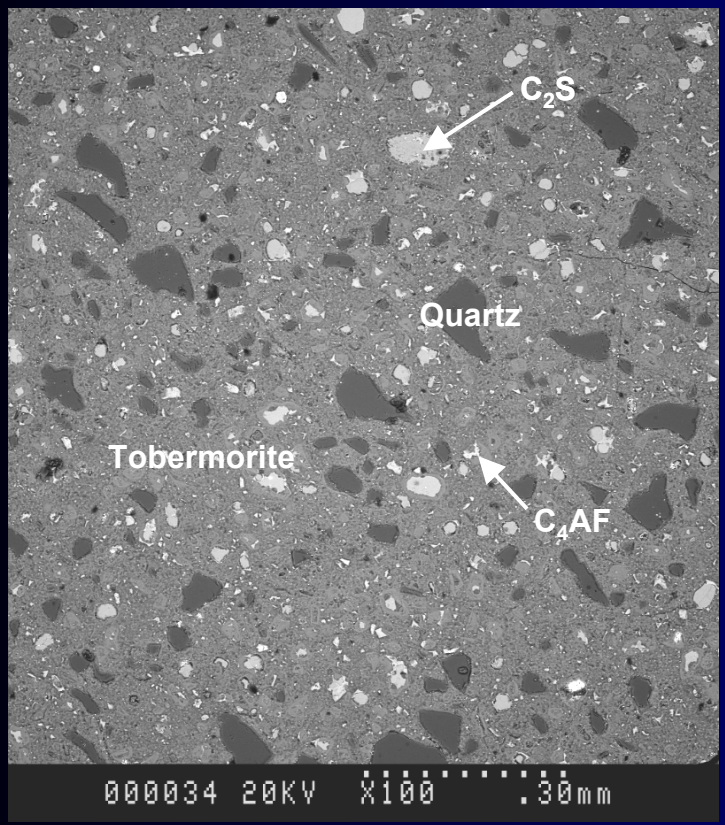
CEMENT (slurry hardening)

- The slurry has a typical composition of well cement slurry :

  Portland class G-HSR + silica flour (quartz grains) + water

- It hardened in hydrothermal conditions during the cure:

  210 bar, 140°C, 8 days



- Assemblage of Tobermorite + Quartz
- Porosity = 0.4

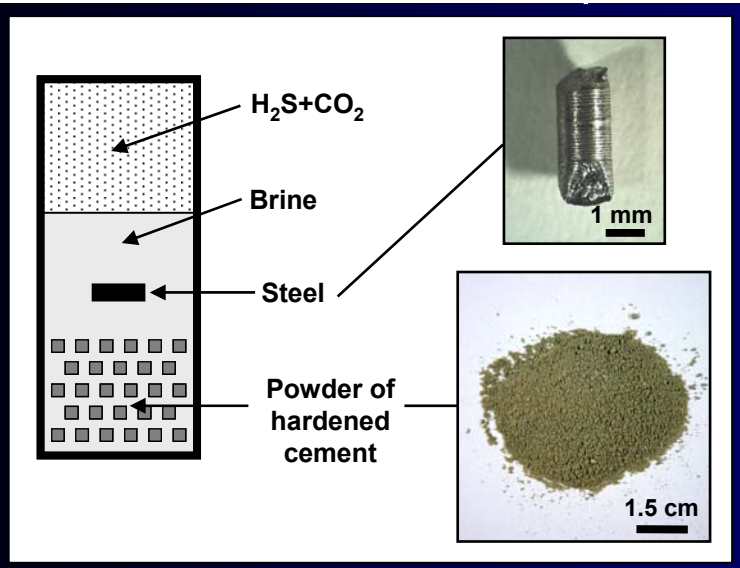
STEEL:

- used for the casing
- low C content

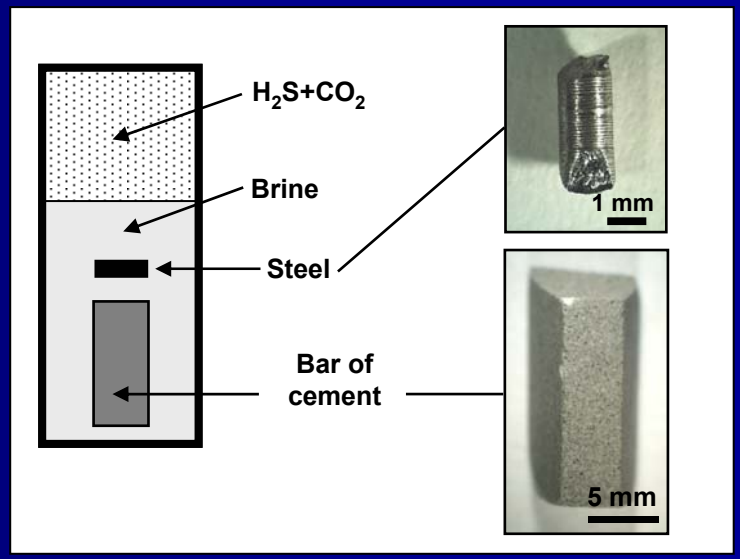
--> Fe° (98 mol%)

Two forms of cement and geological relevant conditions

Cement under the form of powder



Cement under the form of bar



- **Optimisation of the reactive surface --> homogeneous reactivity AND advanced reaction state**
- **Proper minerals reactivity**

"Real" texture of the well cement

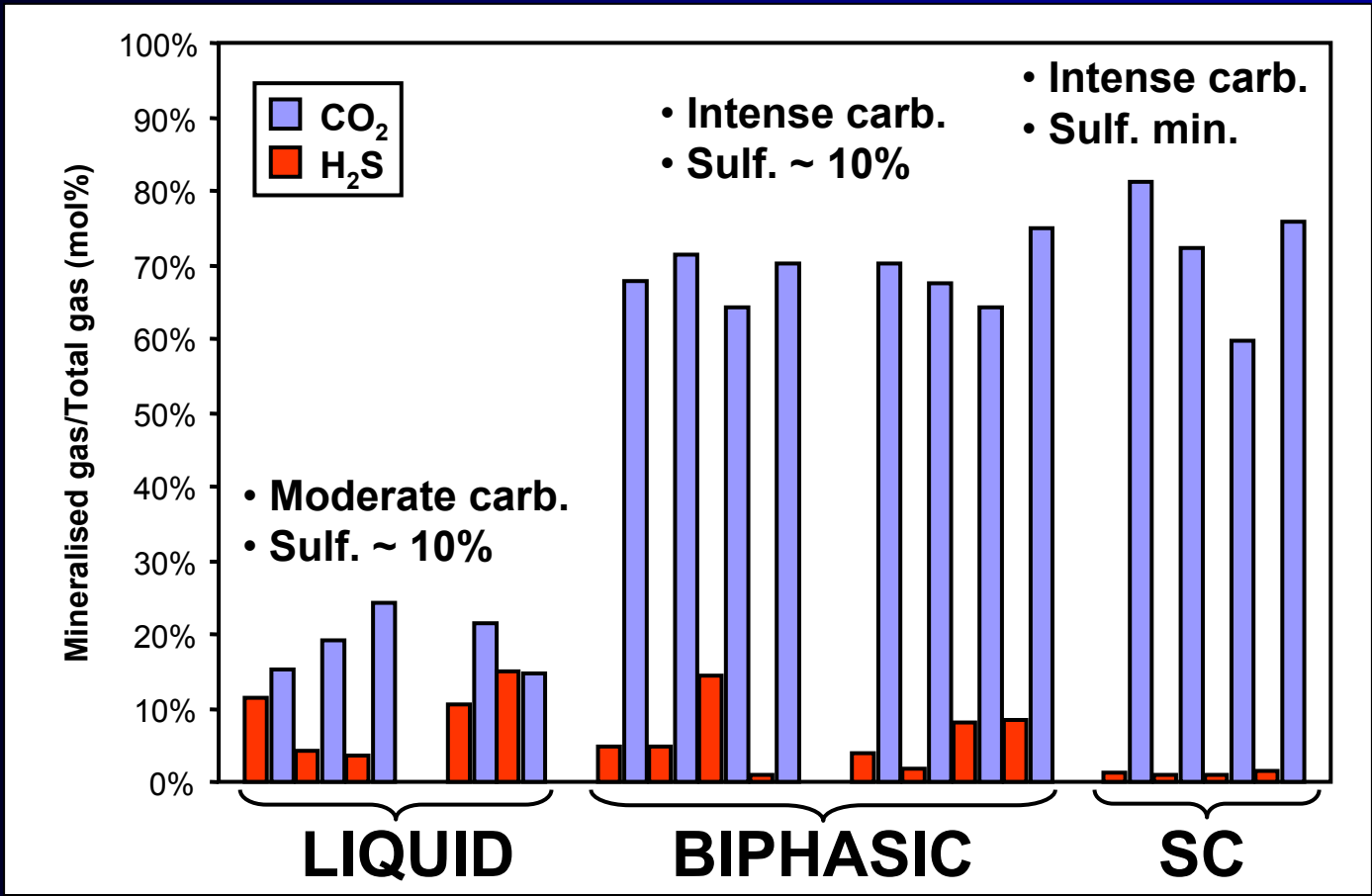
RESERVOIR ⟺ EXPERIMENTATION (times from 15 to 60 days)

- **FORMATION WATER:** NaCl brine (150 g/l)
- **TOTAL PRESSURE:** 500 bar
- **TEMPERATURE:** 120°C, 200°C
- **GAS:** 66mol% H_2S + 34mol% CO_2

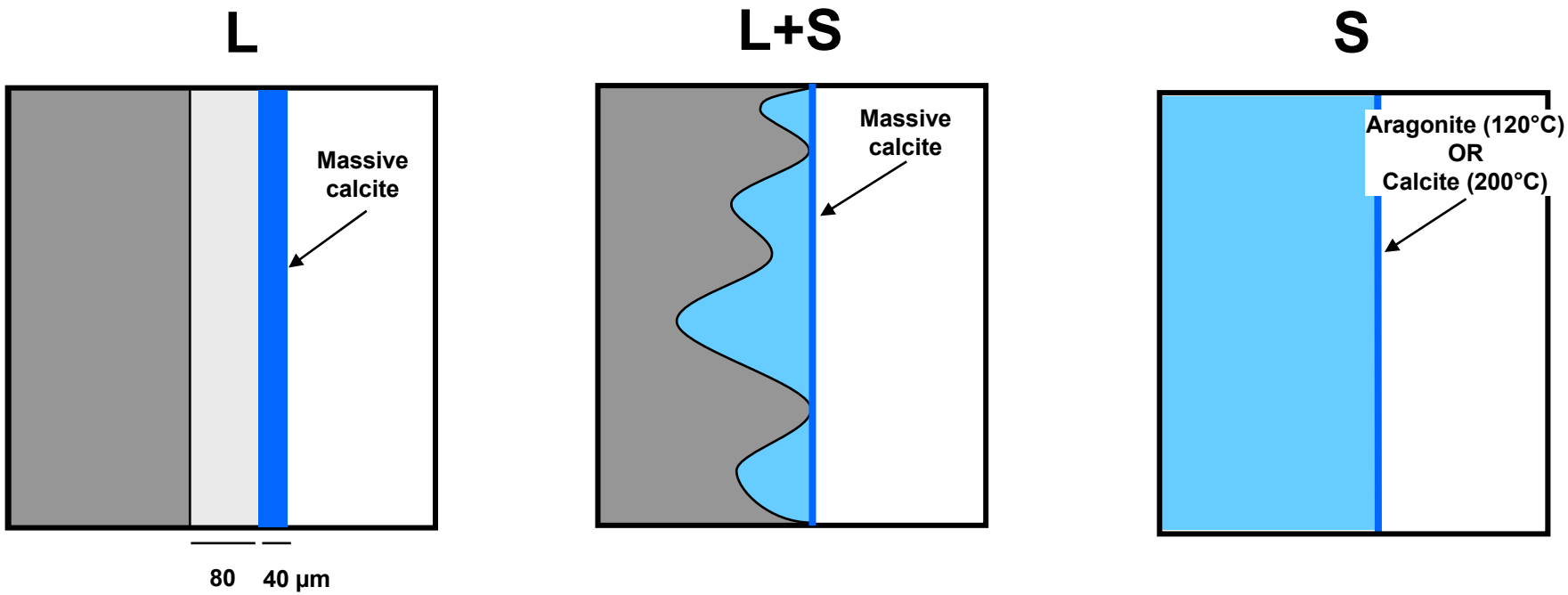
Two degrees of carbonation and sulfidation

SIMPLIFIED REACTIONS:

- Carbonation: $CaO.SiO_2.H_2O + CO_2 \rightarrow CaCO_3 + SiO_2.H_2O$
- Sulfidation: $Fe° + H_2S \rightarrow FeS + H_2$
- $Ca_2AlFeO_5 + 2\ H_2S \rightarrow FeS_2 + \ldots$ (200°C)



Schematization of the alteration profiles



"NO ALTERED" CEMENT
- Hydrothermal CSH
- Quartz (dissolved at 200°C)
- Diffuse calcite

DECALCIFIED CEMENT
- Silica +/- Ca
- Quartz
- Traces of calcite

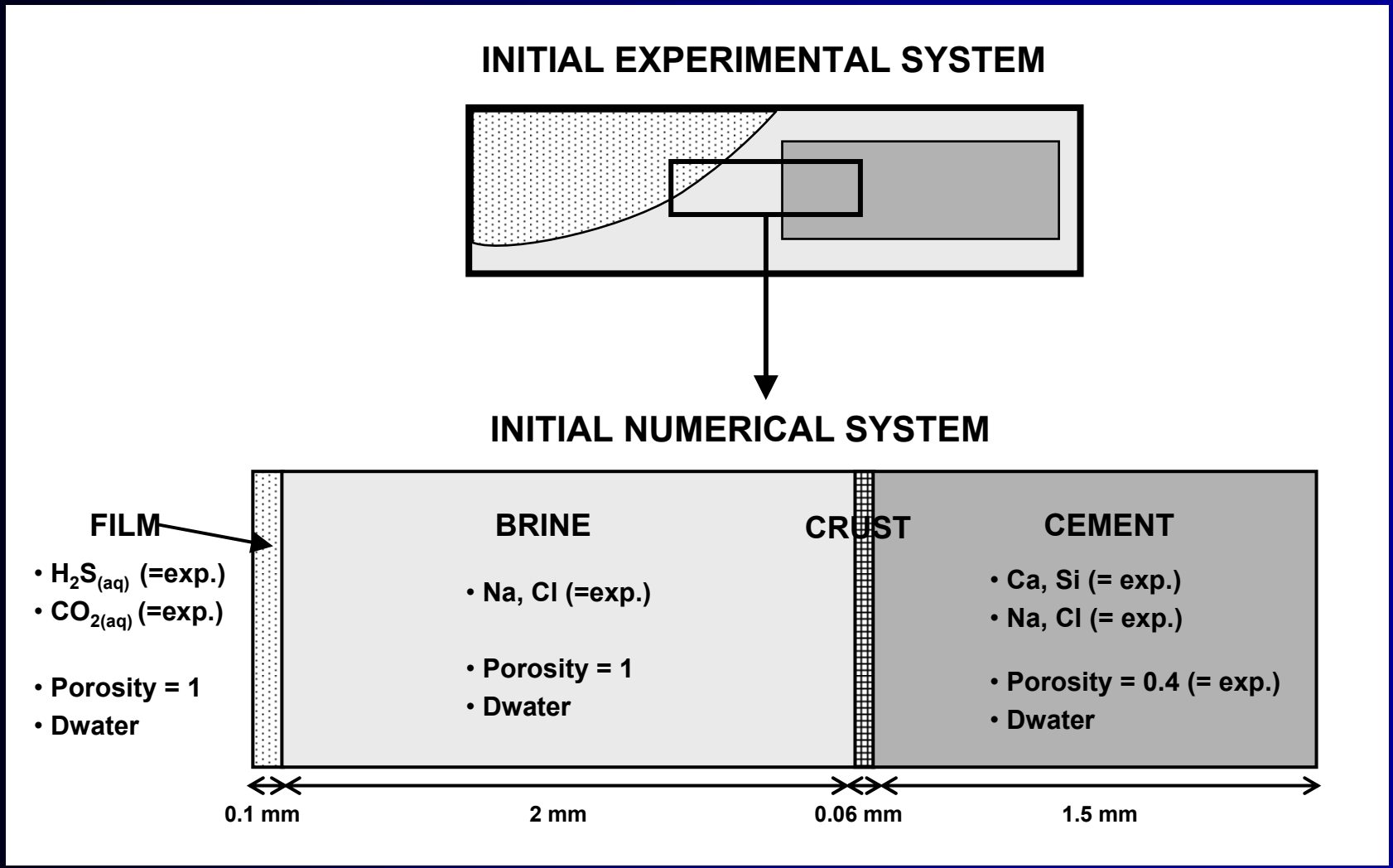
CARBONATED CEMENT
- Silica +/- Ca
- $CaCO_3$ (aragonite+calcite)
- Quartz

Diffusion of C and Ca species
→ Massive deposit of calcite
→ Diffusive blockage
→ Alteration stopping

Intrusion of the SC into the porous volume
→ digitations

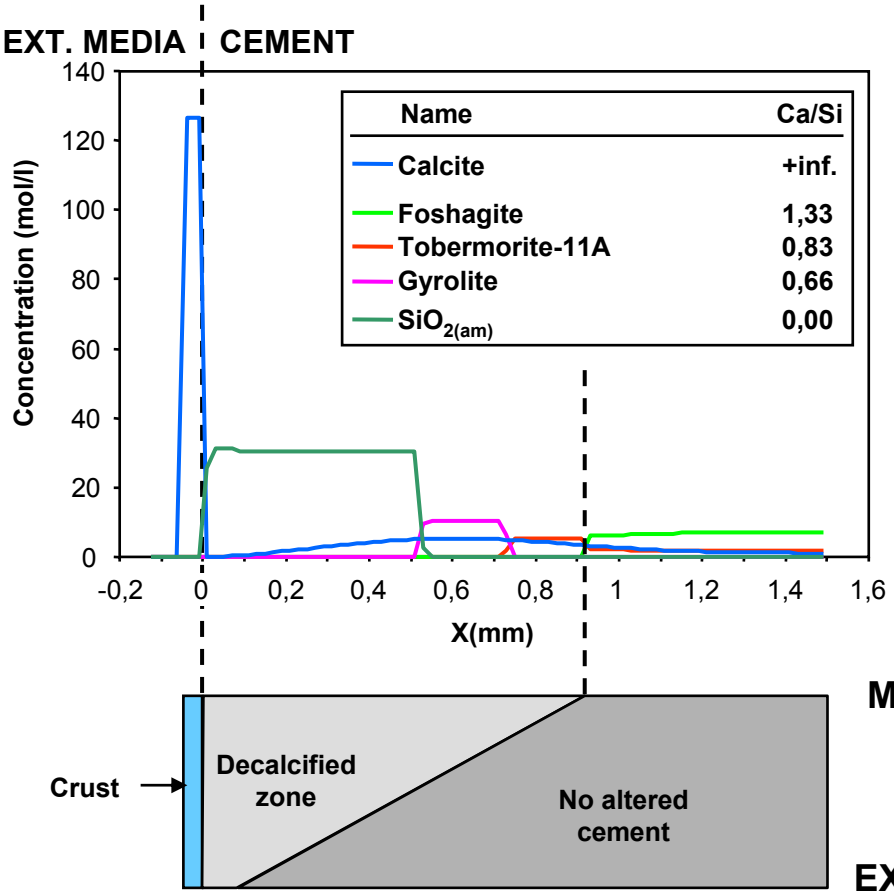
Total carbonation (favorised by the absence of liquid water and optimal diffusion of the SC CO_2)

Analogy experimental system – numerical system

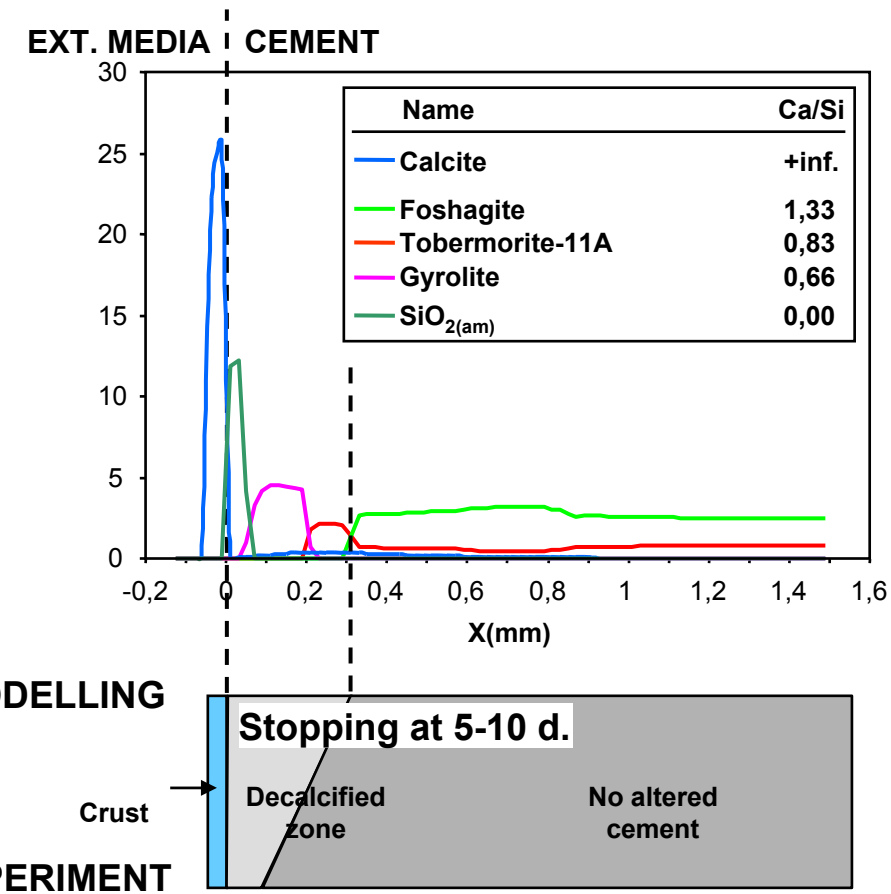


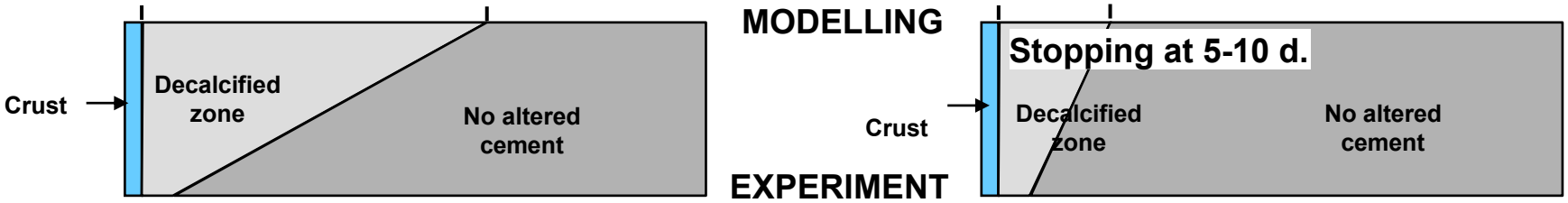
Modelling results

WITHOUT THE DIFFUSIONAL BARRIER EFFECT



WITH THE DIFFUSIONAL BARRIER EFFECT





- Confirm the calcite deposit as the responsible of the stopping of the alteration that we observed experimentally
- Refine the model to fit the experimental and numerical front thicknesses
- Extrapolate this results to large spatial and time scales (well during several 1000 years)