Low pH cements for waste repositories : a review

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Overview

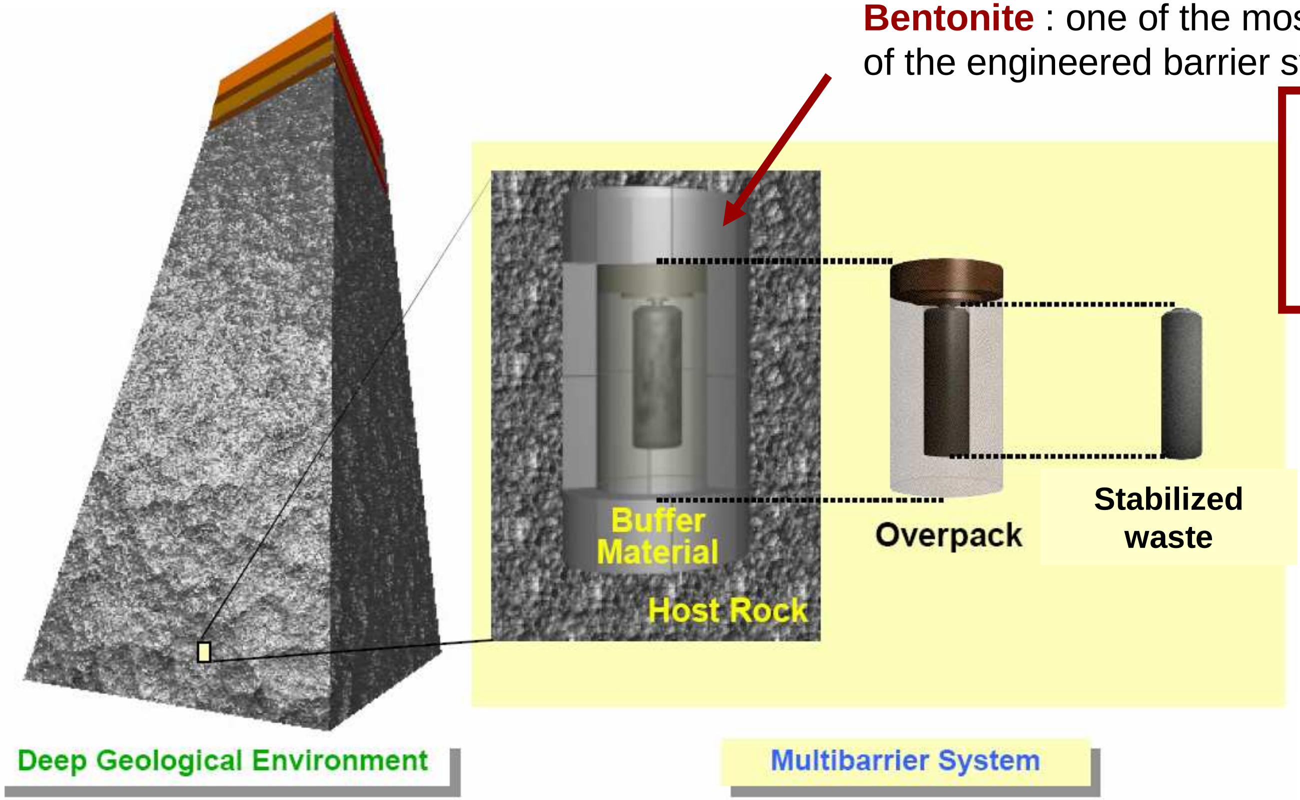
1. Background
2. How to formulate a low pH cement ?
3. Hydration of low-pH cement
4. Properties of low-pH cement-based materials
5. Field experiments
6. Conclusion

1. Background

Modern repository concepts for the disposal of radioactive wastes in deep geological formations are based on a **multi-barrier design approach**.

Bentonite : one of the most safety-critical components of the engineered barrier system

- Good plasticity
- Low hydraulic conductivity
↳ **Unstable at high pH**
- Swelling capacity
- Retention of key radionuclides
- Filtration of colloids



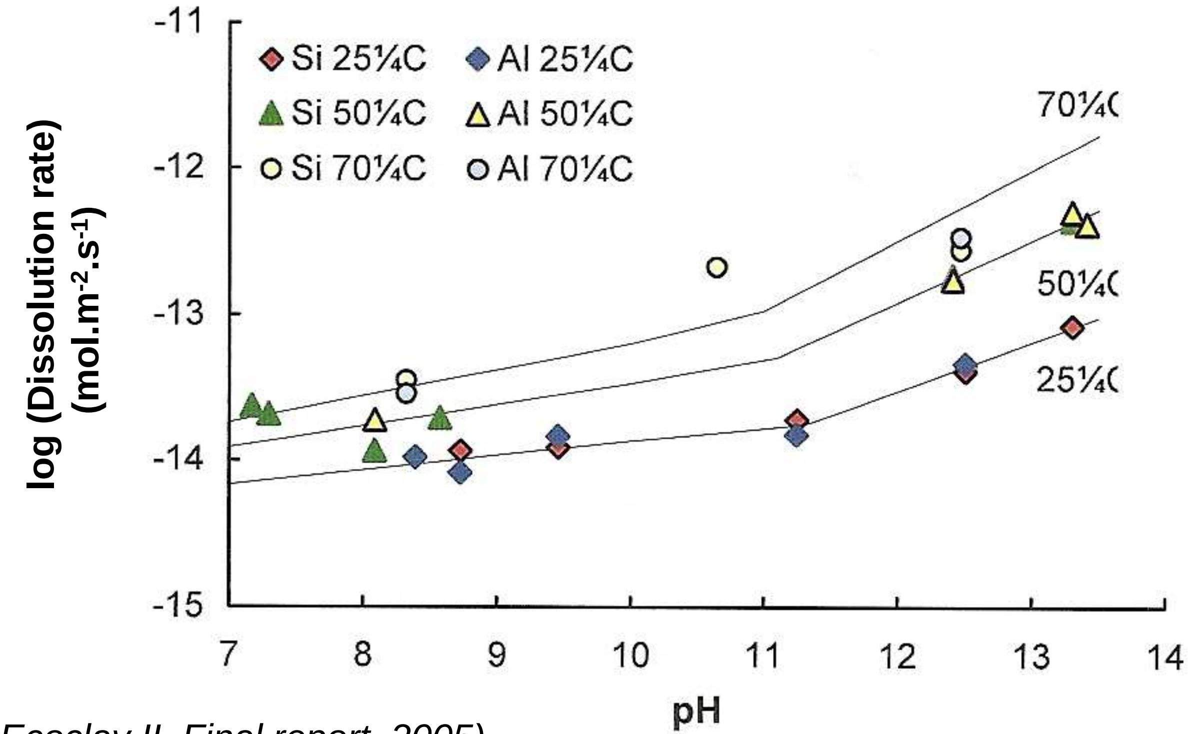
(example of H12, JNC 2000)

1. Background

↳ extensive efforts to better understand the interactions of hyperalkaline fluids with bentonite

↳ investigations aiming at reducing the risk by development of **low pH cement formulations**

1. What does low-pH cement mean?



(Huertas et al, Ecoclay II, Final report, 2005)

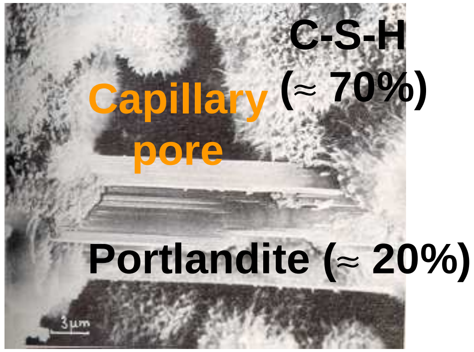
Target for low pH cement-based materials: pore solution pH ≤ 11

In the context of repository engineering: low-pH cement = low-alkalinity cement

2. How to formulate a low-pH cement ?

Hardened paste of Portland cement

➢ **A porous medium**



+ Hydrated aluminates (≈10%)

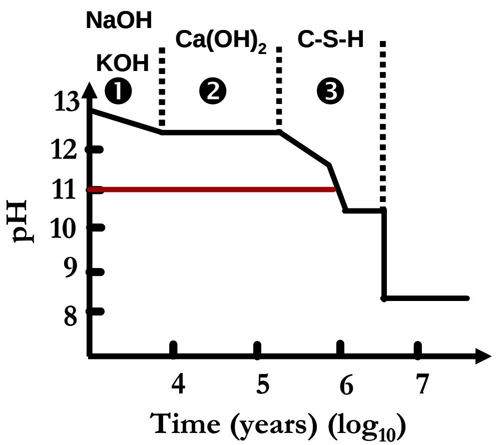
Alkaline pore water

Concentrations in mg/kg of extracted solution

SiO_2	SO_3	Na_2O	K_2O	pH
22	844	4430	26100	13.6

OPC paste (clinker 95.5% - gypsum 4.5%) - W/C 0.5 - curing at 20°C in air-tight bag for 13 months *(Longuet, 1973)*

➢ **The pore solution pH depends on the phases in presence**



Leaching of OPC paste by pure water (Atkinson, 1985)

❶ dissolution of alkalis

❷ dissolution of portlandite

❸ dissolution of C-S-H

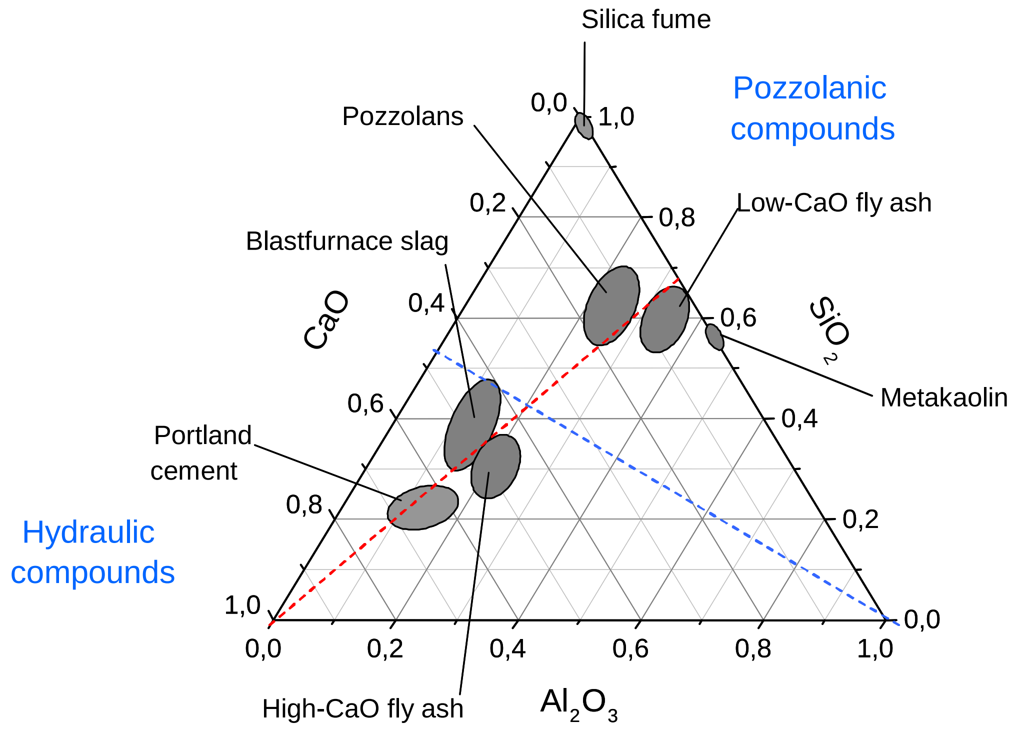
pH = 11 ⇒ C/S of C-S-H ≈ 0.8

2. How to formulate a low-pH cement ?

Blended cement pastes

Interest of a pozzolanic addition :

✓ portlandite consumption : CH + S → C-S-H
✓ OPC dilution
✓ decrease of the Ca/Si ratio of the C-S-H, which decreases their equilibrium pH and enhances their sorption capacity of alkalis (Hong, 1999)



2. How to formulate a low-pH cement ?

The first low-pH concretes

Concrete reference	LHHPC (Gray, 1998)
Cement composition	OPC 50% - SF 50%
Cement content (kg/m^3)	194
W/C	0.5
Aggregates content (kg/m^3)	1935
Sand / coarse aggregates	0.861
Quartzitic filler (kg/m^3)	194
Plasticizer content (% by cement weight)	5.3
Slump after mixing (mm)	-
Temperature rise (adiabatic conditions)	≈20℃
Compressive strength (90 d – MPa)	≈80
Total shrinkage (90 d - µm/m)	-
pH of water equilibrated with crushed material	10.6 (90 d – Water / Solid = 1)

2. How to formulate a low-pH cement ?

The first low-pH concretes

Concrete reference	LHHPC (Gray, 1998)	OSF (or HFSC) (Iriya, 1999)
Cement composition	OPC 50% - SF 50%	OPC 40% - SF 20% - FA 40%
Cement content (kg/m^3)	194	500
W/C	0.5	0.3
Aggregates content (kg/m^3)	1935	1656
Sand / coarse aggregates	0.861	1.208
Quartzitic filler (kg/m^3)	194	-
Plasticizer content (% by cement weight)	5.3	3
Slump after mixing (mm)	-	72.5
Temperature rise (adiabatic conditions)	≈20℃	50.2℃
Compressive strength (90 d – MPa)	≈80	106
Total shrinkage (90 d - µm/m)	-	-516
pH of water equilibrated with crushed material	10.6 (90 d – Water / Solid = 1)	11 (28 d – Water / Solid = 40)

2. How to formulate a low-pH cement ?

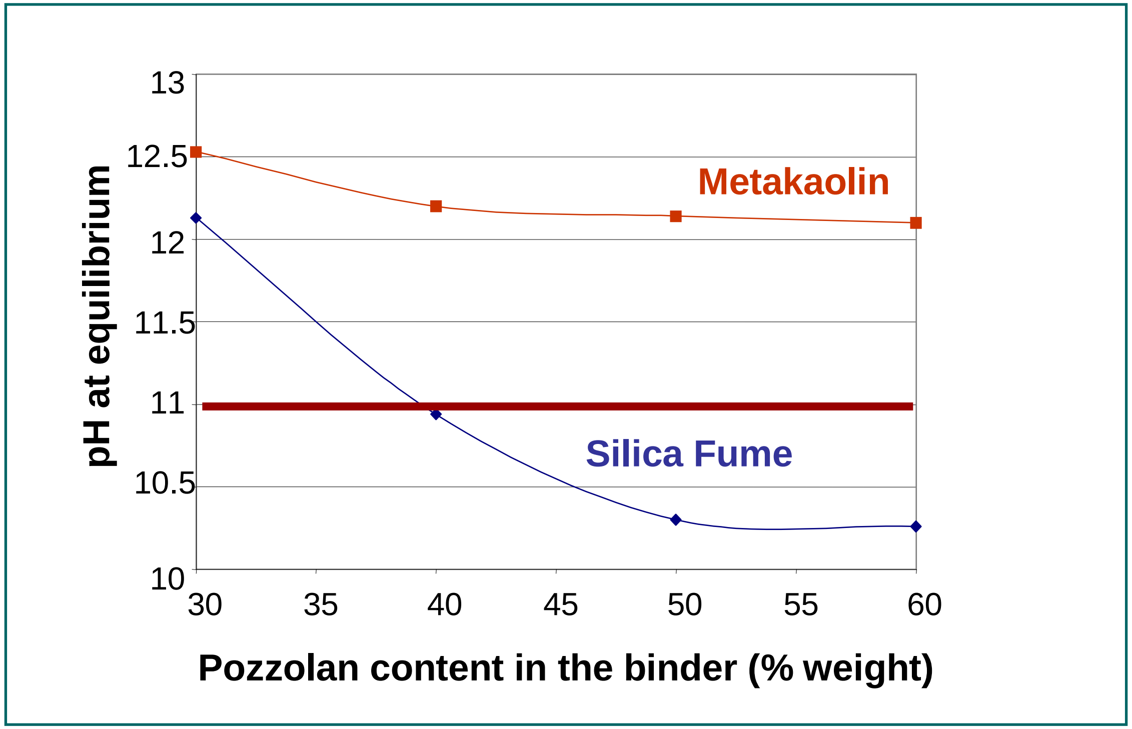
The first low-pH concretes

Concrete reference	LHHPC (Gray, 1998)	OSF (or HFSC) (Iriya, 1999)	36F (Lagerblad, 2003)
Cement composition	OPC 50% - SF 50%	OPC 40% - SF 20% - FA 40%	OPC 83.3% - SF 16.7%
Cement content (kg/m^3)	194	500	180
W/C	0.5	0.3	0.82
Aggregates content (kg/m^3)	1935	1656	2005.5
Sand / coarse aggregates	0.861	1.208	1.900
Quartzitic filler (kg/m^3)	194	-	200
Plasticizer content (% by cement weight)	5.3	3	1.2
Slump after mixing (mm)	-	72.5	450
Temperature rise (adiabatic conditions)	≈20°C	50.2°C	-
Compressive strength (90 d – MPa)	≈80	106	55
Total shrinkage (90 d - µm/m)	-	-516	≈-500
pH of water equilibrated with crushed material	10.6 (90 d – Water / Solid = 1)	11 (28 d – Water / Solid = 40)	11.7 (28 d – Water / Solid = 1.675)

2. How to formulate a low-pH cement ?

Investigation of OPC/SF and OPC/MK blends

Equilibrium pH of fully-hydrated cement suspensions (L/S = 9 mL/g)



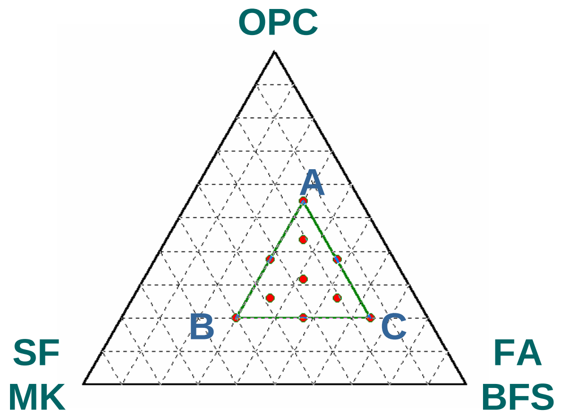
pH < 11 ⇒ silica fume content ≥ 40%

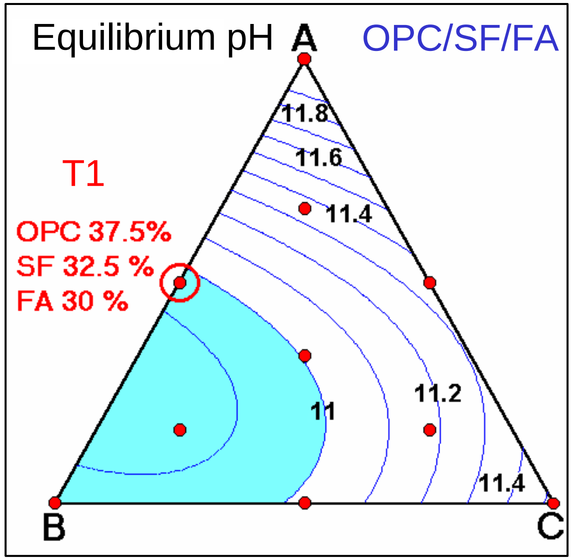
(Cau Dit Coumes, 2003)

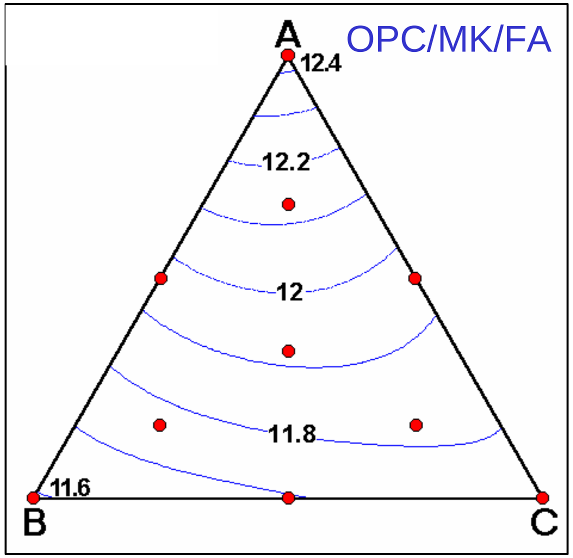
2. How to formulate a low-pH cement ?

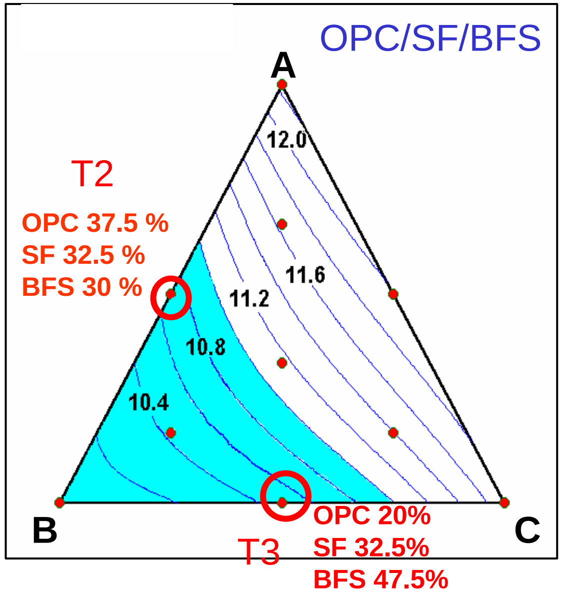
Investigation of OPC/SF/FA, OPC/MK/FA and OPC/SF/BFS blends

OPC : 20 - 55%
SF or MK : 15 - 50%
FA or BFS : 30 - 65%





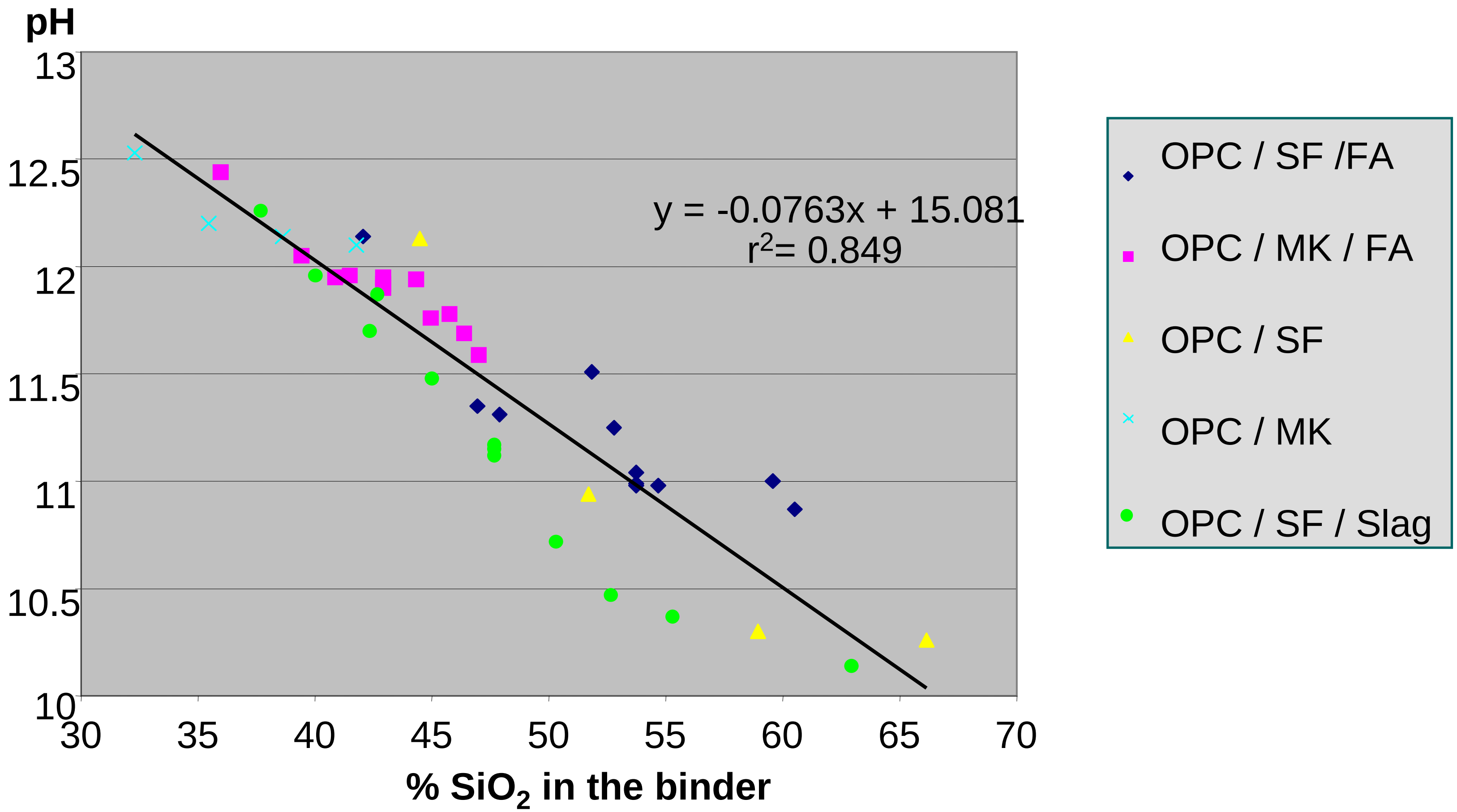




(Cau Dit Coumes, 2003)

2. How to formulate a low-pH cement ?

Investigation of OPC/SF, OPC/MK, OPC/SF/FA, OPC/MK/FA and OPC/SF/BFS blends



A key parameter: the SiO_2 content of the binder

(Cau Dit Coumes, 2003)

2. How to formulate a low-pH cement ?

Low-pH cements currently under investigation

Country	Cement composition	Developed materials	Authors
Canada - AECL	**OPC 50% - SF 50%**	High strength concrete	Martino et al.
Finland – Posiva Oy	**OPC 60% - SF 40 %**	Injection grout	Vuorio et al.
France – ANDRA, CEA, EDF	**OPC 60% - SF 40 %** **OPC 37.5% - SF 32.5 % - FA 30%** **OPC 20% - SF 32.5 % - BFS 47.5 %** **OPC 33% - BFS 13.5 % - FA 13.5 % - SF 40%**	High strength concrete	Codina et al.
Japan – JAEA, CRIEPI, NUMO	**OPC 40% - SF 20% - FA 40%**	Shotcrete High strength concrete (cast in place or pre-cast)	Nishiuchi et al. Kobayashi et al.
USA - ORNL	**OPC 40% - BFS 30 % - FA 25 % - SF 5%**	Shotcrete High strength concrete	Dole et al.
Spain – IETcc-CSIC, ENRESA	**OPC 60% - SF 40 %** **OPC 35 % - SF 35 % - FA 30%**	Shotcrete	Garcia et al.
Switzerland, NAGRA	**OPC 60% - SF 40 %**	Shotcrete	Fries et al.

(3rd workshop on low-pH cement for a geological repository, Paris, 2007)

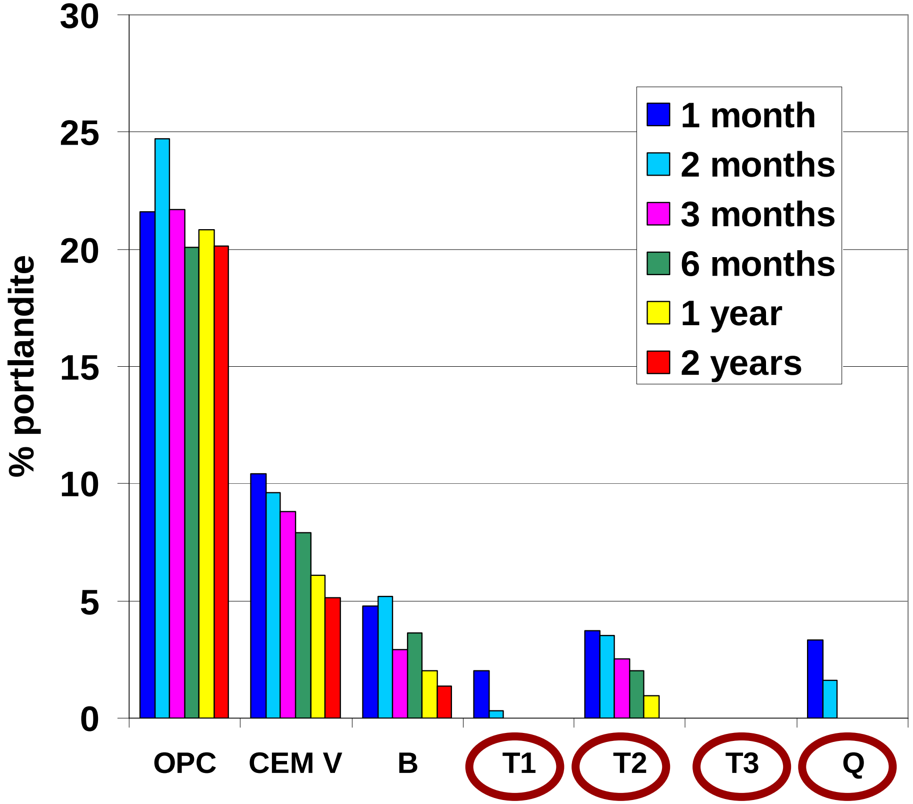
http://www.esdred.info/medias/Mod5-WP2-D4_ProceedingsLowpHWorkshop_27Aug07.pdf

3. Hydration of low-pH cement

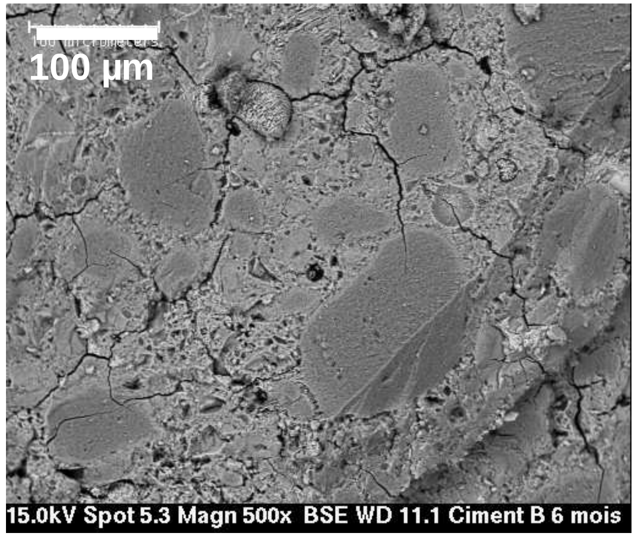
Mineralogy

Ref.	OPC	SF	FA	Slag
B	60%	40%		
T1	37.5%	32.5%	30%	
T2	37.5%	32.5%		30%
T3	20%	32.5%		47.5%
Q	33.6%	40%	13.2%	13.2%

Investigations on cement pastes (W/C = 0.5)



Portlandite content measured by TGA/DTA



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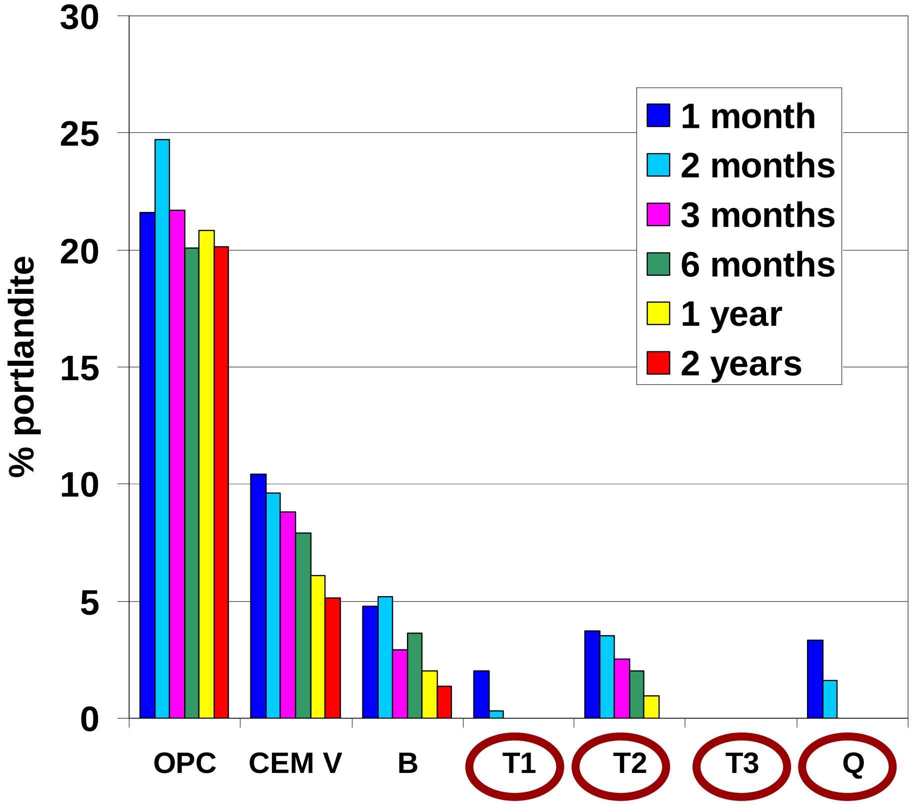


Portlandite content measured by TGA/DTA

Investigations on cement pastes (W/C = 0.5)

XRD

<u>Hydrates in 2–years old cement pastes</u>

B : C-S-H, portlandite, ettringite
T1: C-S-H, ettringite
T2, T3, Q: C-S-H, ettringite, hydrotalcite

	Ca/Si		Al/Ca	
	6 m	16 m	6 m	16 m
B	1.7	1.5	-	-
T1	1.4	1.2	0.095	-
T3	1.3	1.0	0.026	0.069

(Codina et al., 2007)

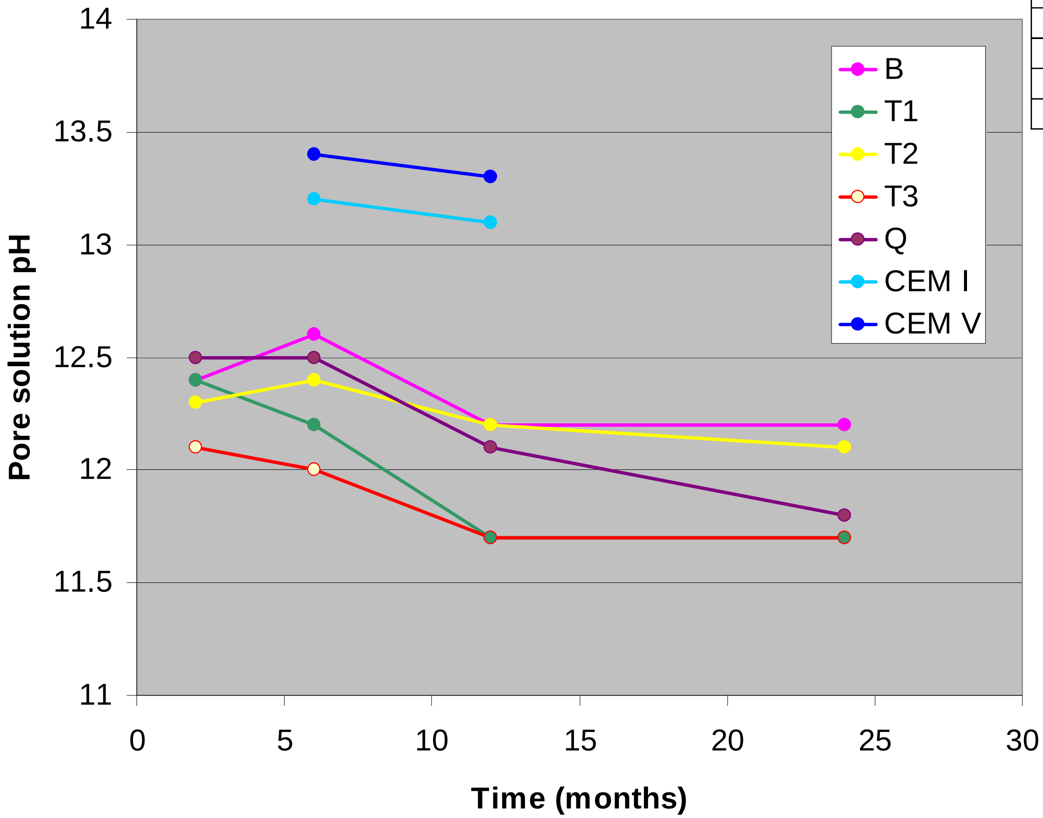
Hydrated pastes of B and T'1 (OPC 35%, SF 35%, FA 30%)
0.8 ≤ Ca/Si ≤ 1.2

(Garcia et al., 2007)

3. Hydration of low-pH cement

Pore solution chemistry

Pore solution extraction



Ref.	OPC	SF	FA	Slag
B	60%	40%		
T1	37.5%	32.5%	30%	
T2	37.5%	32.5%		30%
T3	20%	32.5%		47.5%
Q	33.6%	40%	13.2%	13.2%

(Codina et al., 2007)

➢ The pore solution pH values of pastes B, T1, T2, T3 and Q are reduced by more than one unit as compared to OPC and CEMV cements

Hydration of low-pH cement

Pore solution chemistry

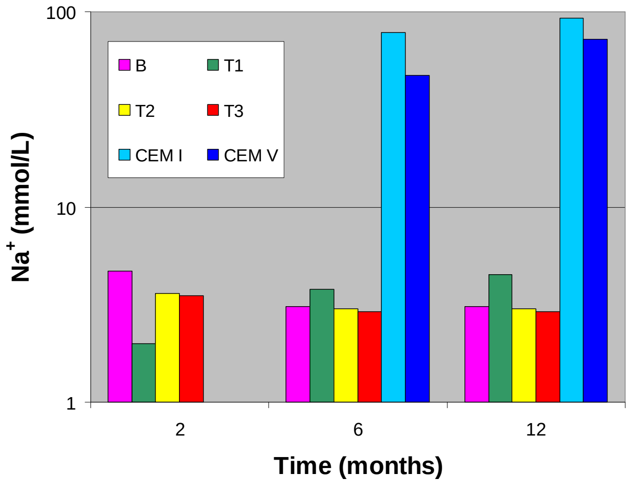
	Pore solution pH	
Cement composition	**Cement paste (24 month-old)**	**Concrete (20 month-old)**
B (60% OPC – 40% SF)	12.3 ± 0.1	11.4 ± 0.2
T1 (37.5% OPC – 32.5% SF – 30% FA)	11.7 ± 0.1	11.0 ± 0.3
T2 (37.5% OPC – 32.5% SF – 30% BFS)	12.1 ± 0.1	11.3 ± 0.2
T3 (20% OPC – 32.5% SF – 47.5% BFS)	11.7 ± 0.1	11.0 ± 0.1

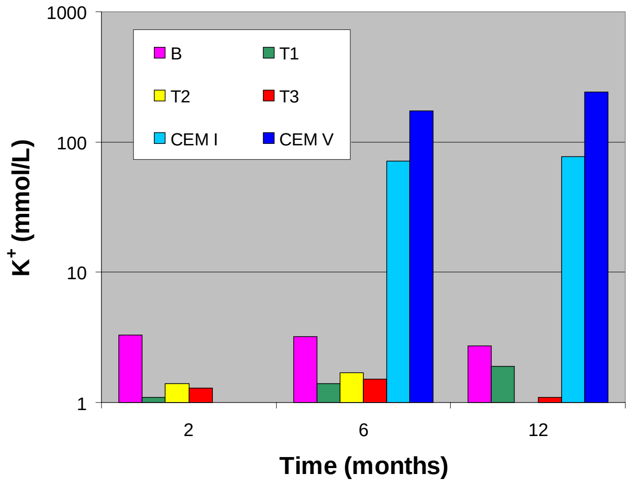
(Codina et al., 2007)

Better SF dispersion in concrete than in cement paste

3. Hydration of low-pH cement

Pore solution chemistry





Strong reduction of the Na^+ and K^+ content (by a factor 20 to 200) in the extracted pore solution of low-pH cement pastes as compared to OPC and CEM V

Ref.	OPC	SF	FA	Slag
B	60%	40%		
T1	37.5%	32.5%	30%	
T2	37.5%	32.5%		30%
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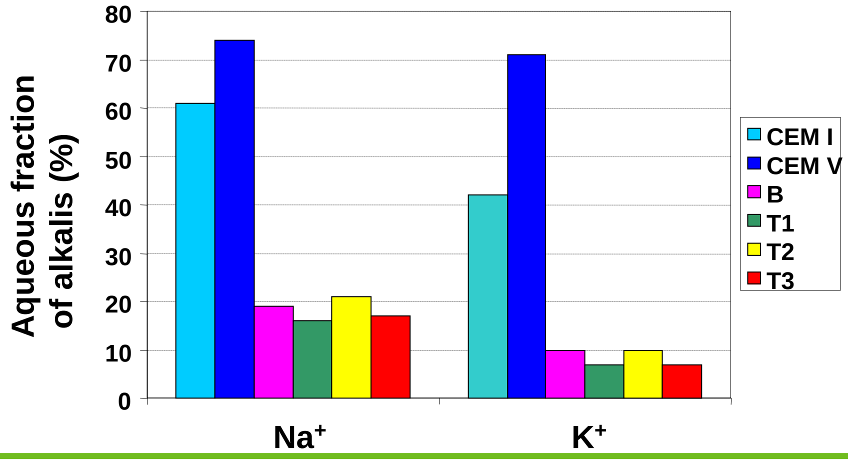
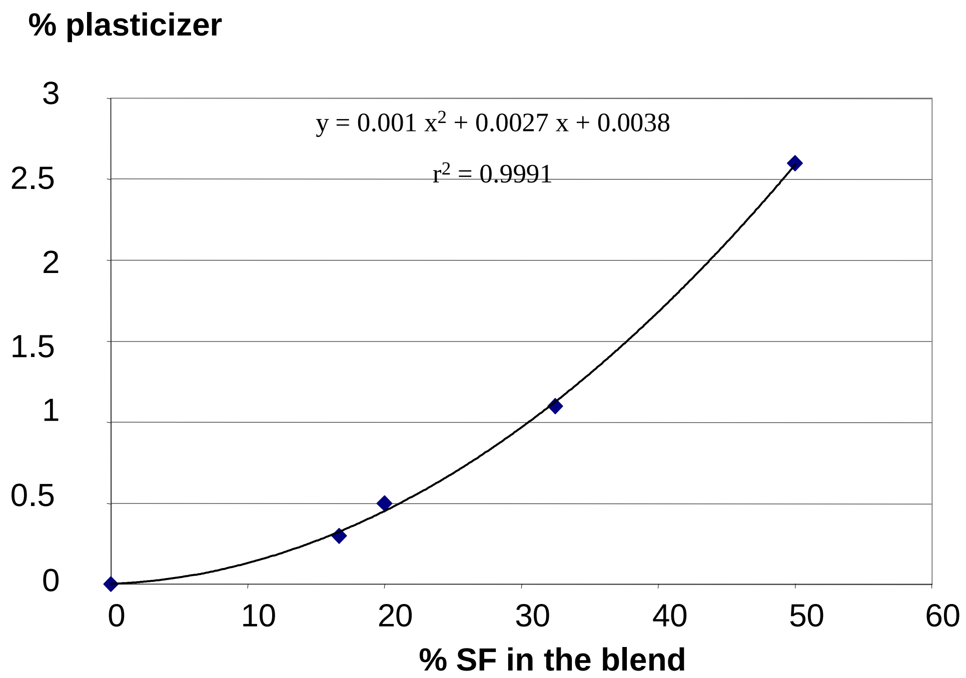


(Codina et al, 2007)

4. Properties of low-pH cement-based materials

Workability after mixing



Standardized mortars
(W/C = 0.5, S/C = 3)

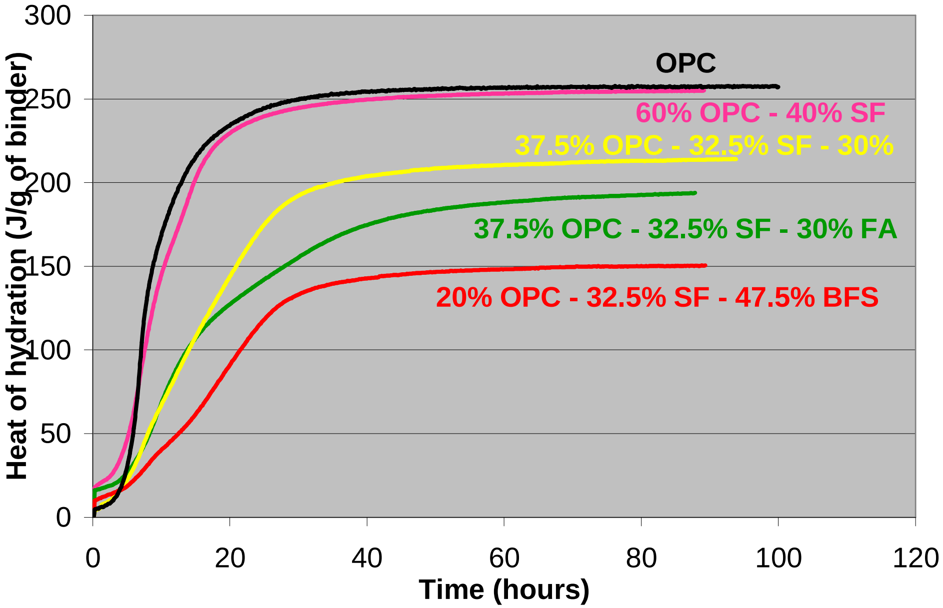
(Cau Dit Coumes, 2006)

Strong increase in the grout viscosity with the SF content of the blend

↳ necessary use of superplasticizers to get workable materials
↳ experiments under way to assess the potential of these organic additives to form strong complexes with radionuclides *(Snellman, 2007) (Yamamoto, 2007)*

4. Properties of low-pH cement-based materials

Heat of hydration



Langavant semi-adiabatic calorimetry
Standardized mortars
(W/C = 0.5 – S/C = 0.3)

(Codina et al., 2006)

➯ Possibility to design low-heat concrete

Temperature rise	Lab tests	$20m^3$ blocks
LHHPC concrete (OPC 50 % - SF 50% ; 194 kg/m^3)	16°C	21°C
High-performance concrete (OPC 91% - SF 9%; 547 kg/m^3)	45°C	-
High fly ash concrete (OPC 50% - FA 50%; 388 kg/m^3)	-	42°C

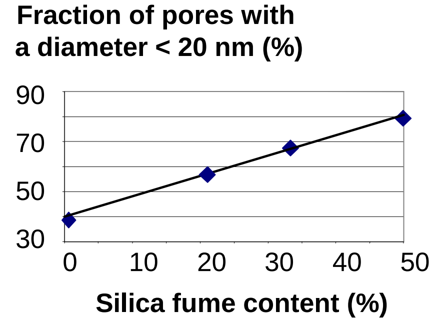
(Gray et al, 1998)

4. Properties of low-pH cement-based materials

Porosity and mechanical strength

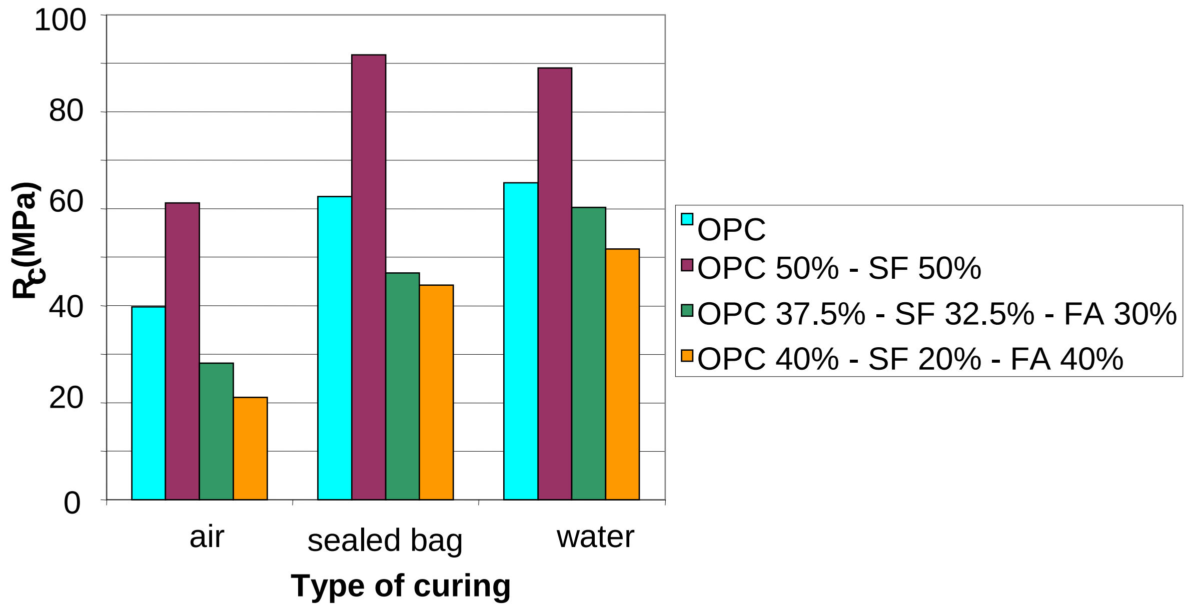
Blend	OPC 50% SF 50%	OPC 37.5% SF 32.5% FA 30%	OPC 40% SF 20% FA 40%	OPC 100%
Total porosity (%)	14.3	20.0	22.0	14.1
Porosity below 20 nm (% of total porosity)	75.5	67.6	57.9	38.9

1 year of curing under water



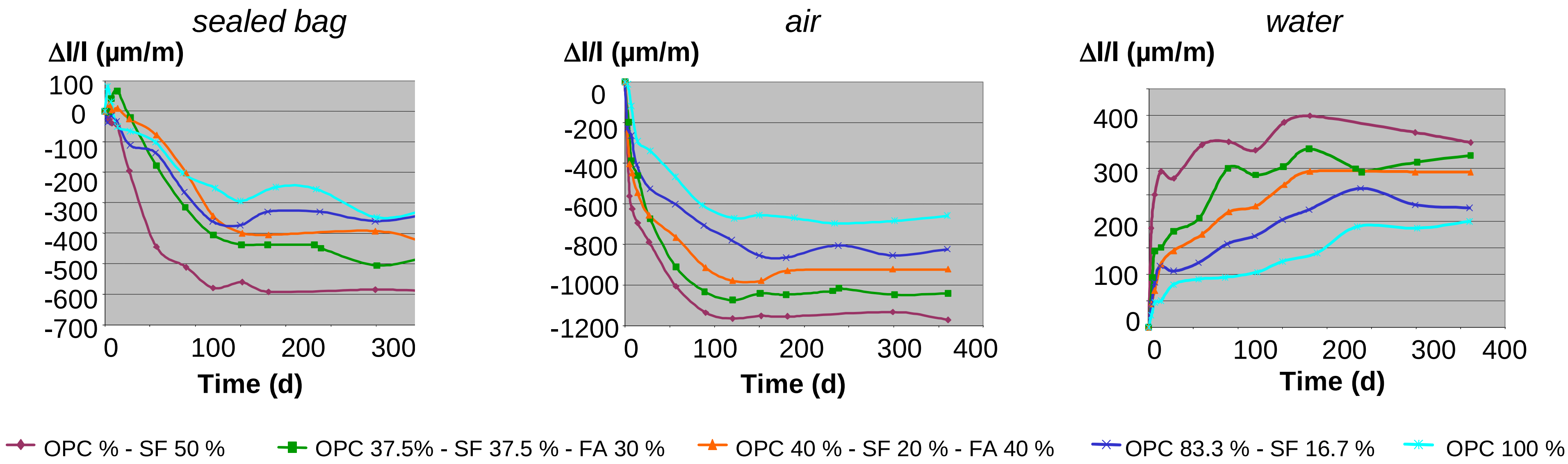
↳ Refinement of the porosity with the SF content of the blend

Compressive strength of standardized mortars (W/C = 0.5, S/C = 3) 1 year of curing



4. Properties of low-pH cement-based materials

Dimensional stability



↳ The dimensional instability increased with the SF content

- **Shrinkage at early age (4 – 24 h)**

(Codina et al, 2007)

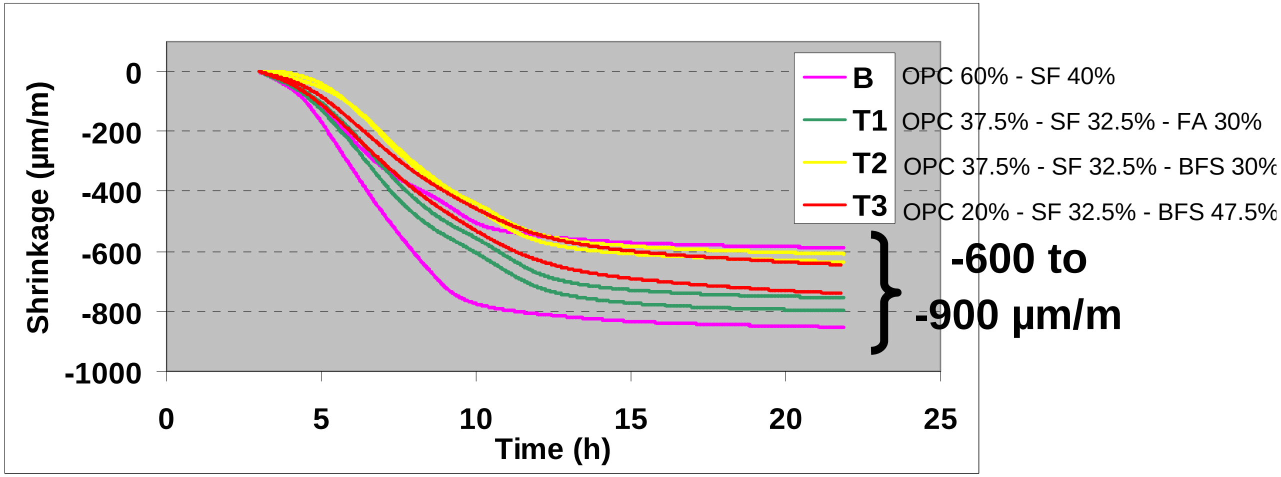
<u>Self-leveling concrete</u>

440 ≤ C ≤ 500 kg/m³

0,4 ≤ E/L ≤ 0,44

↳ -1000 à -1150 µm/m

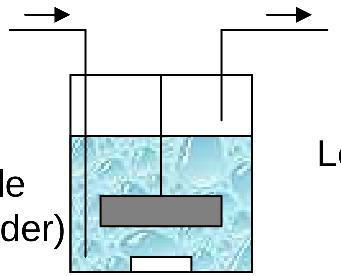
(Turcry et Loukili, 2004)



4. Durability of low-pH cement-based materials

Most experiments: static leaching tests ; diffusion-controlled release

N_2



Low-pH sample
(alternative: powder)

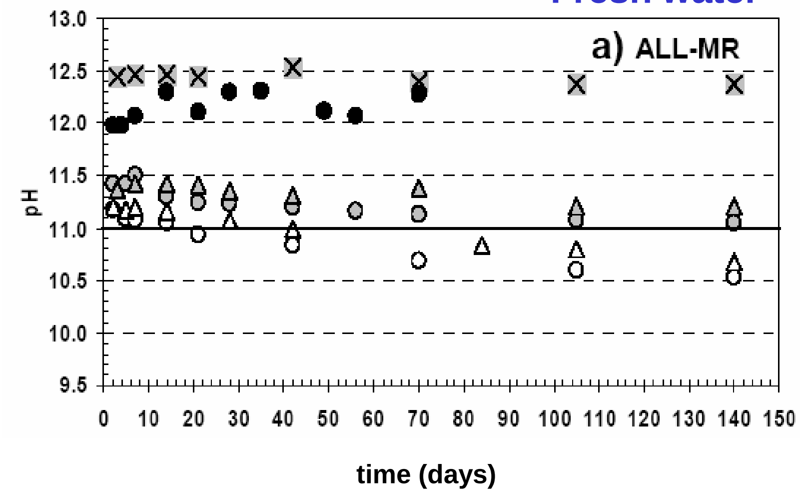
Magnetic stirring

Renewal of leaching solution once equilibrium is reached

Leaching solution: demineralized water
simulated groundwater solutions (saline / fresh)

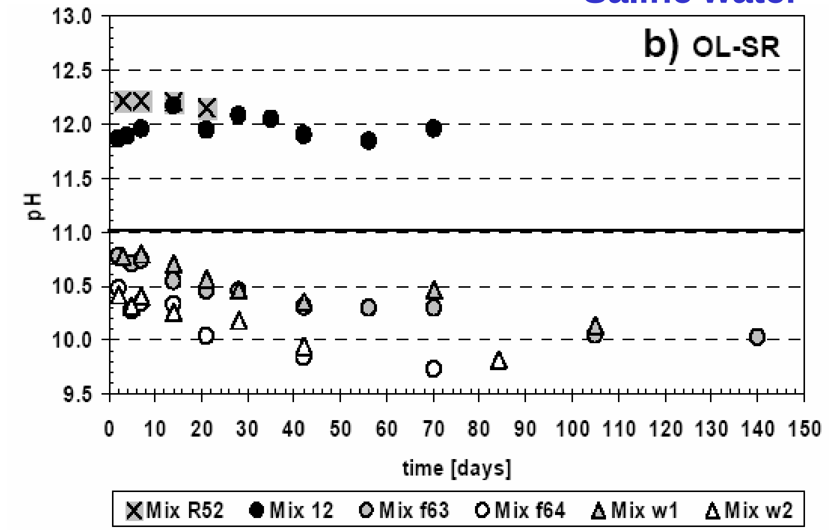
(Vuorinen et al, 2005), (Vuorio et al, 2007), (Yamamoto et al, 2007)

Fresh water



(Vuorinen et al, 2005)

Saline water



%SF 7% 23% 38% 46% 38% (WCE) 46% (WCE)

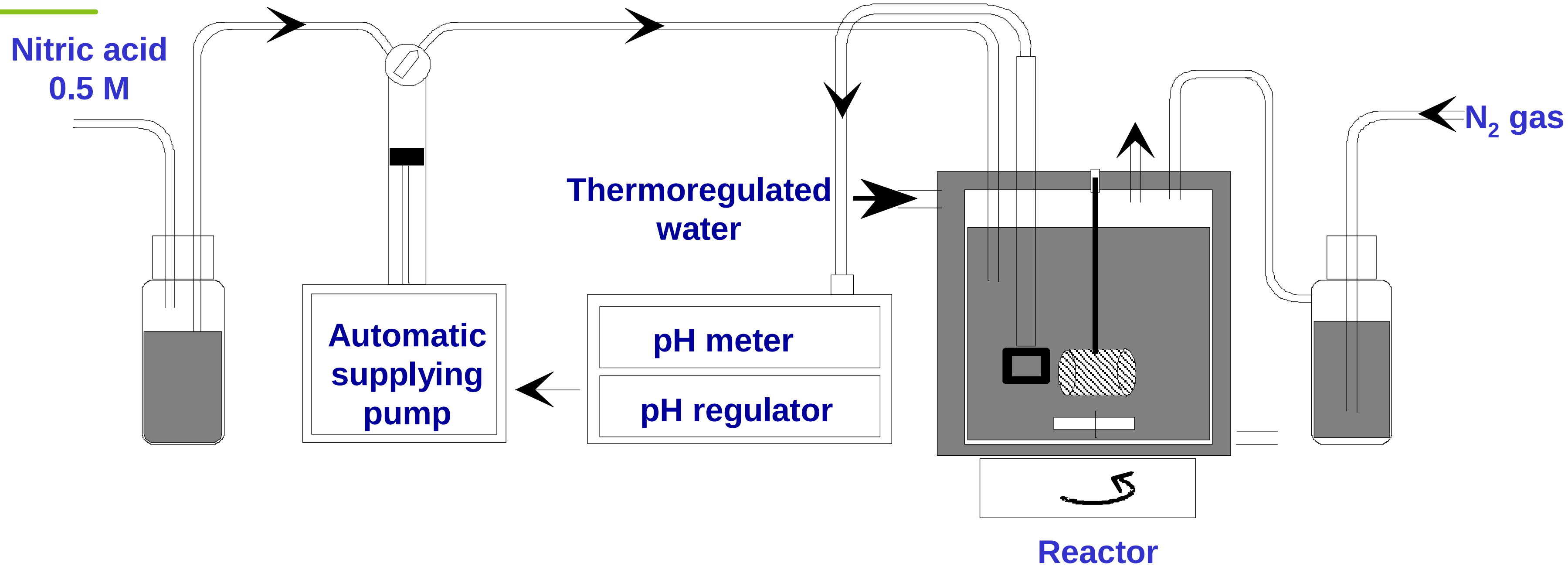
➢ Temptative modelling (Owada et al., 1999): overestimation of pH after extensive leaching, underestimation of [Ca] at earlier stages

4. Durability of low-pH cement-based materials

Leaching at constant pH

Experimental device

(Galle et al, 2002)
(Codina et al, 2007)



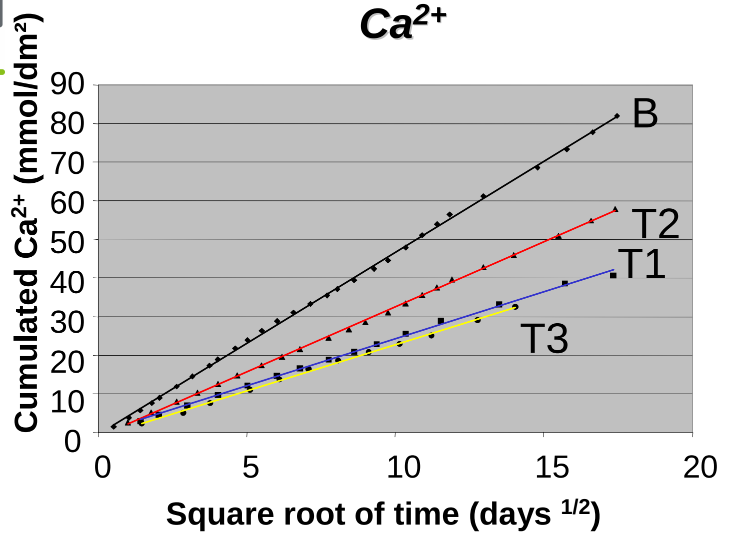
- constant temperature (20℃) and pH (7)
- stirring and injection of N_2 into the cells to avoid carbonation
- samples protected from lateral attack by polymer coating
- renewal of the solution in connection with the quantity of added HNO_3

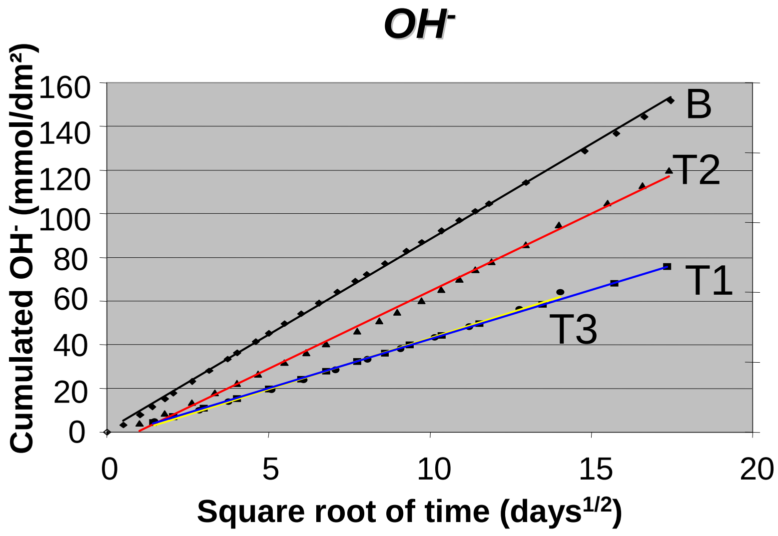
4. Durability of low-pH cement-based materials

Leaching at constant pH

Analysis of the leachate

Ref.	OPC	SF	FA	Slag
B	60%	40%		
T1	37.5%	32.5%	30%	
T2	37.5%	32.5%		30%
T3	20%	32.5%		47.5%





Cement paste	Decalcification rate ($mmol/dm^2/day^{0.5}$)
B	4.71 ± 0.02
T_2	3.36 ± 0.02
T_1	2.44 ± 0.03
T_3	2.39 ± 0.03
OPC	13 ± 2
CEM V	3.0 ± 0.4

4. Durability of low-pH cement-based materials

Leaching at constant pH

Analysis of the leachate

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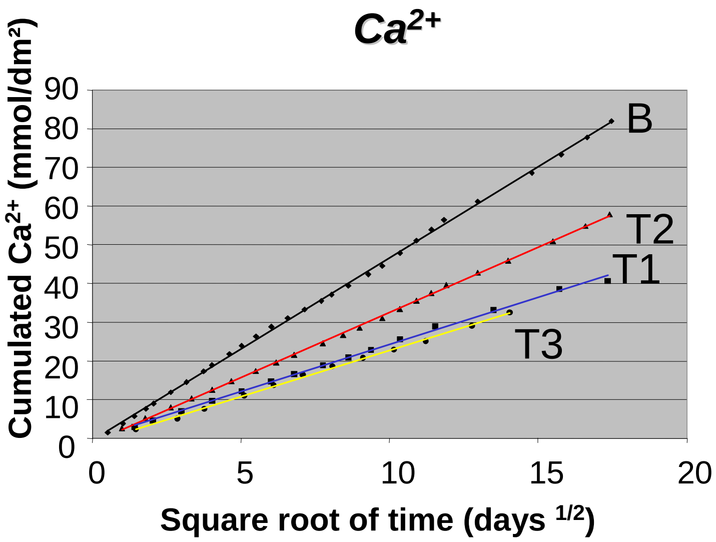

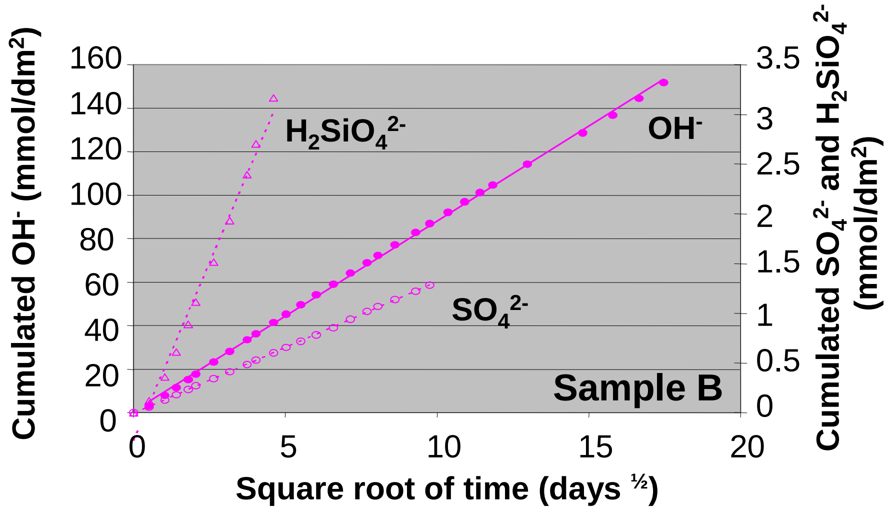

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T_3	2.39 ± 0.03
OPC	13 ± 2
CEM V	3.0 ± 0.4

Balance of the Ca^{2+} flux by the release of :

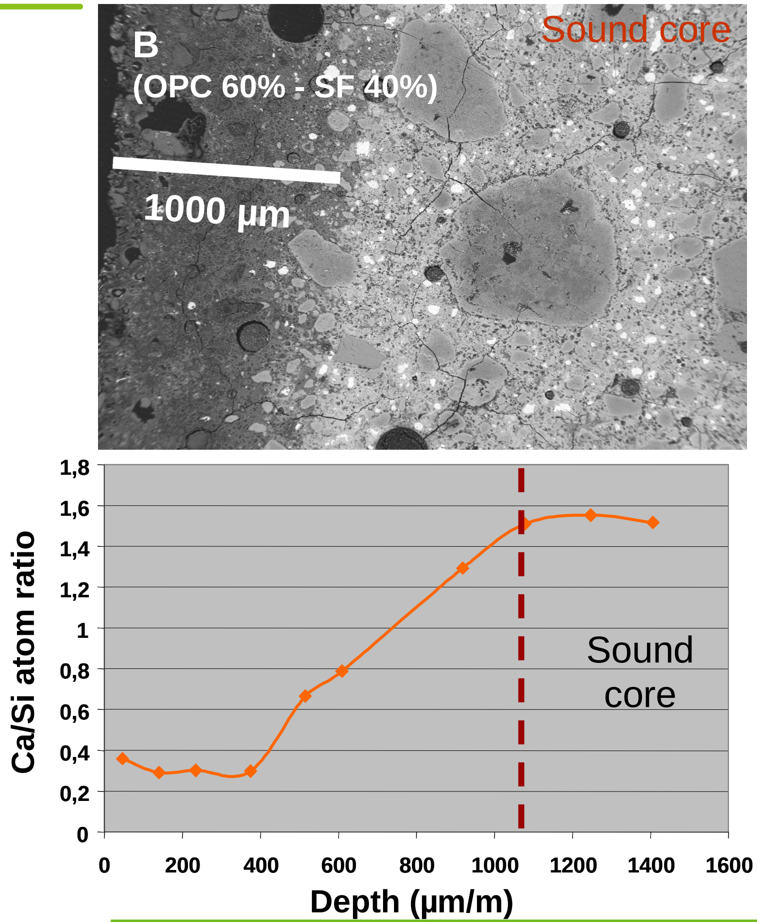
- OH^-
- SO_4^{2-}
- $H_2SiO_4^{2-}$

4. Durability of low-pH cement-based materials

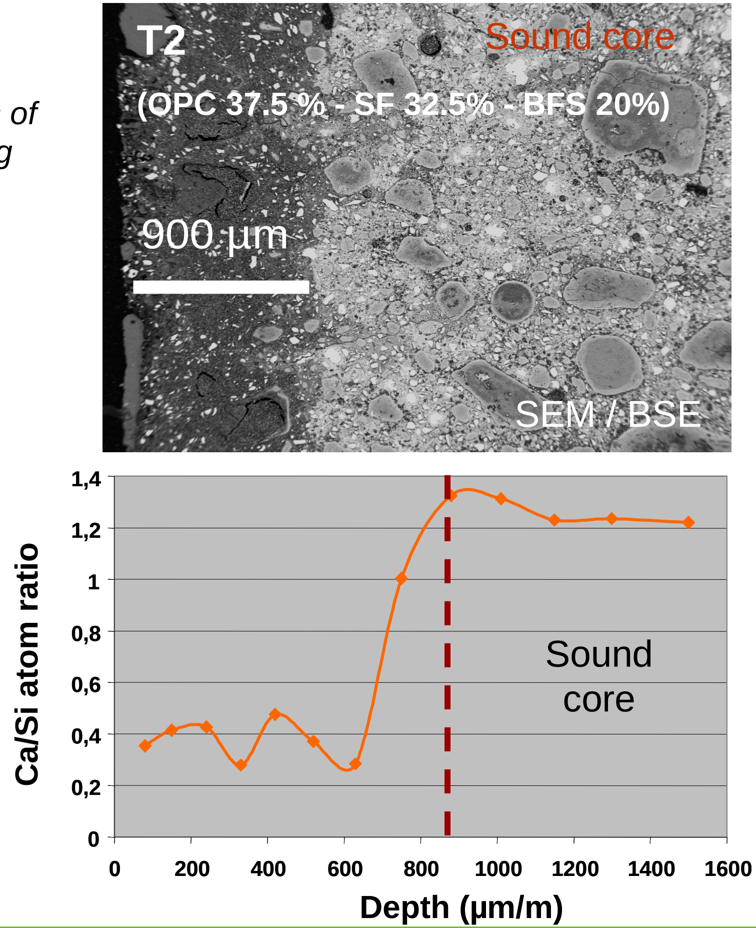
Leaching at constant pH

Analysis of the solid

How to determine the location of the degradation front for portlandite-free materials ?



4 months of leaching



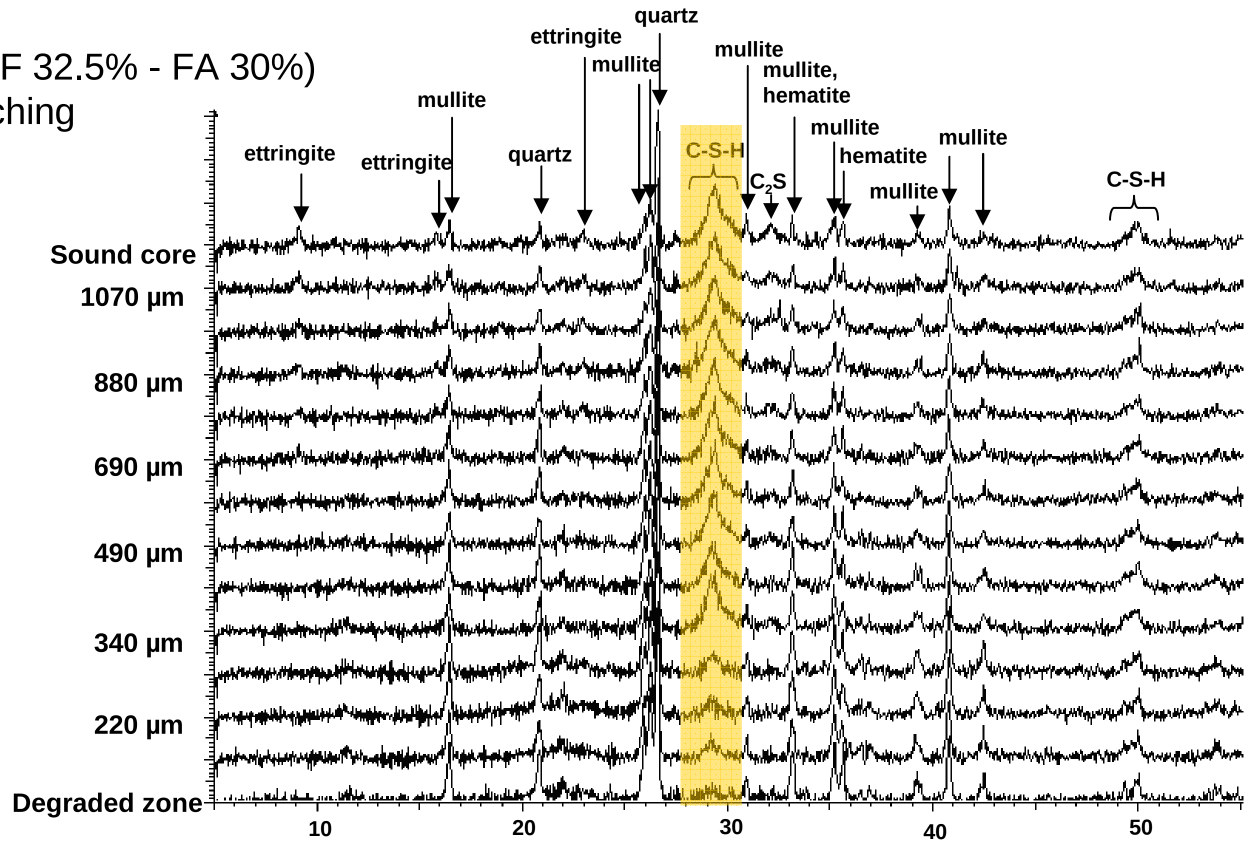
4. Durability of low-pH cement-based materials

Leaching at constant pH

Analysis of the solid

How to determine the location of the degradation front for portlandite-free materials ?

T1
(OPC 37.5% - SF 32.5% - FA 30%)
4 months of leaching



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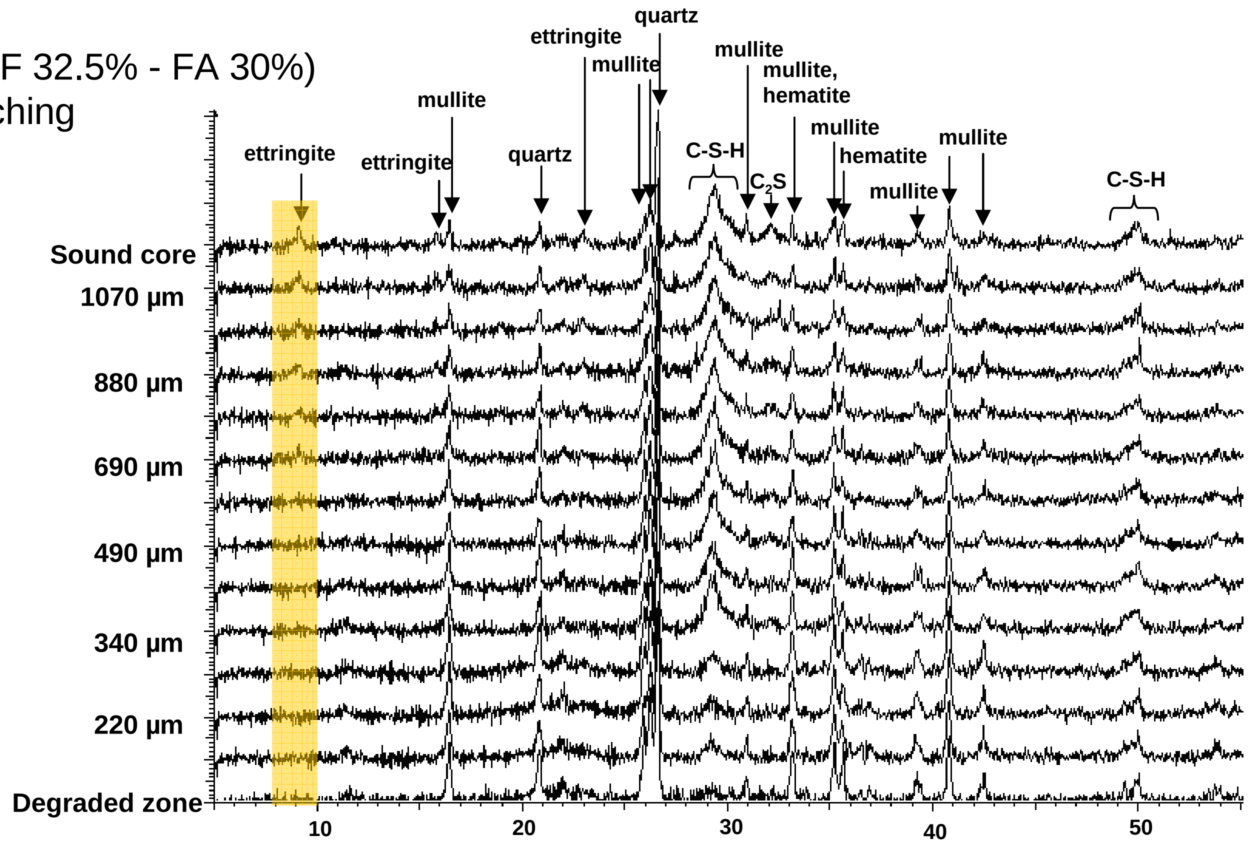

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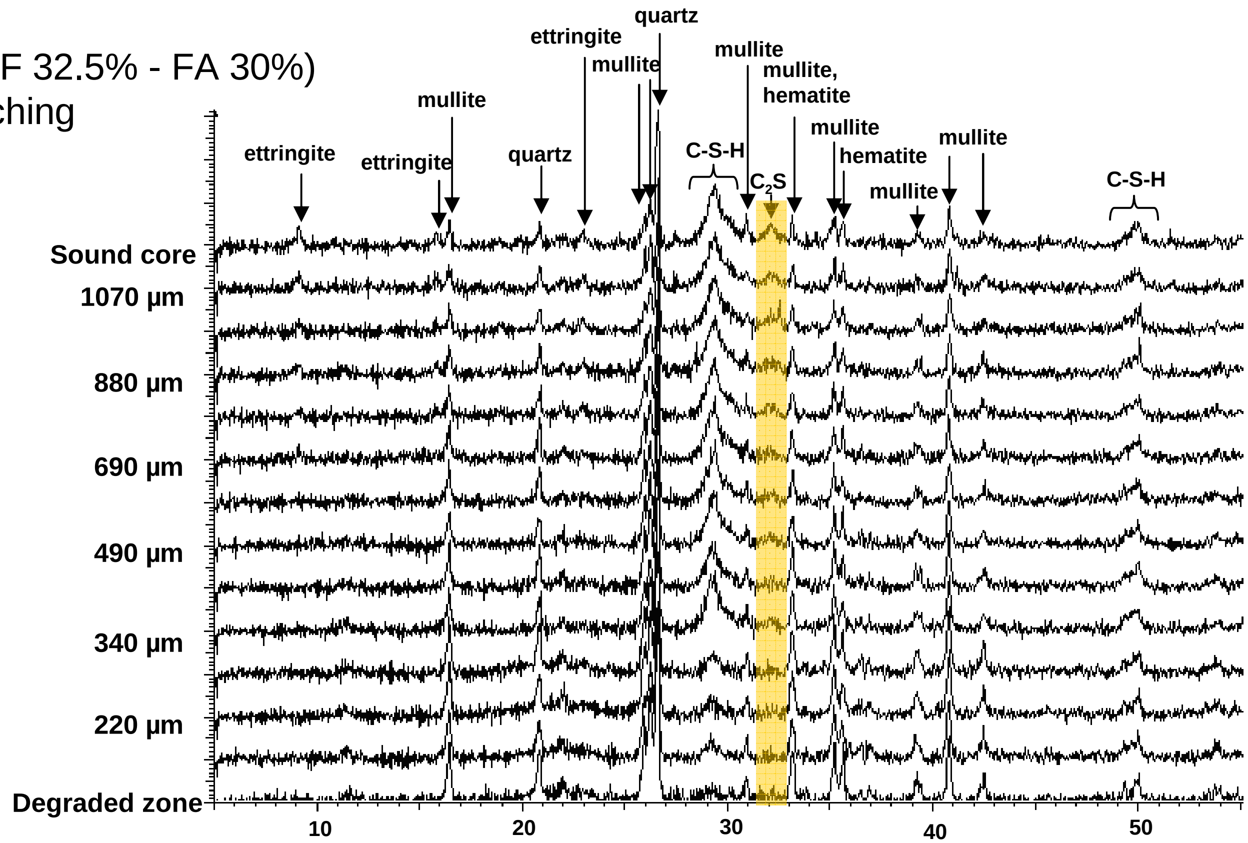


4. Durability of low-pH cement-based materials

Leaching at constant pH

Reactive transport model (HYTEC)

Input data

- Composition of the solid (mineralogy inferred from XRD, TGA/DTA and SEM, amount of each phase calculated)
- Porosity (derived from experiment and calculated $\{1-V_{molar}(\text{hydrates})\}$
- External conditions (pH 7, T = 20°C, leached concentrations maintained to zero in the external solution)

Adjusted parameters

- Diffusion coefficient (D)
- Evolution of D with porosity (empirical law of Archie)

Output data

- Ca^{2+}, $H_2SiO_3^-$, SO_4^{2-}, OH^- fluxes
- pH
- depth of degraded zone

Modelled experiments

Leaching of cement pastes (W/C = 0.5)

- B: OPC 60% - SF 40% (C-S-H 1.5 + ettringite)
- T1: OPC 37.5% - SF 32.5% - FA 30% (C-S-H 1.1 + ettringite)

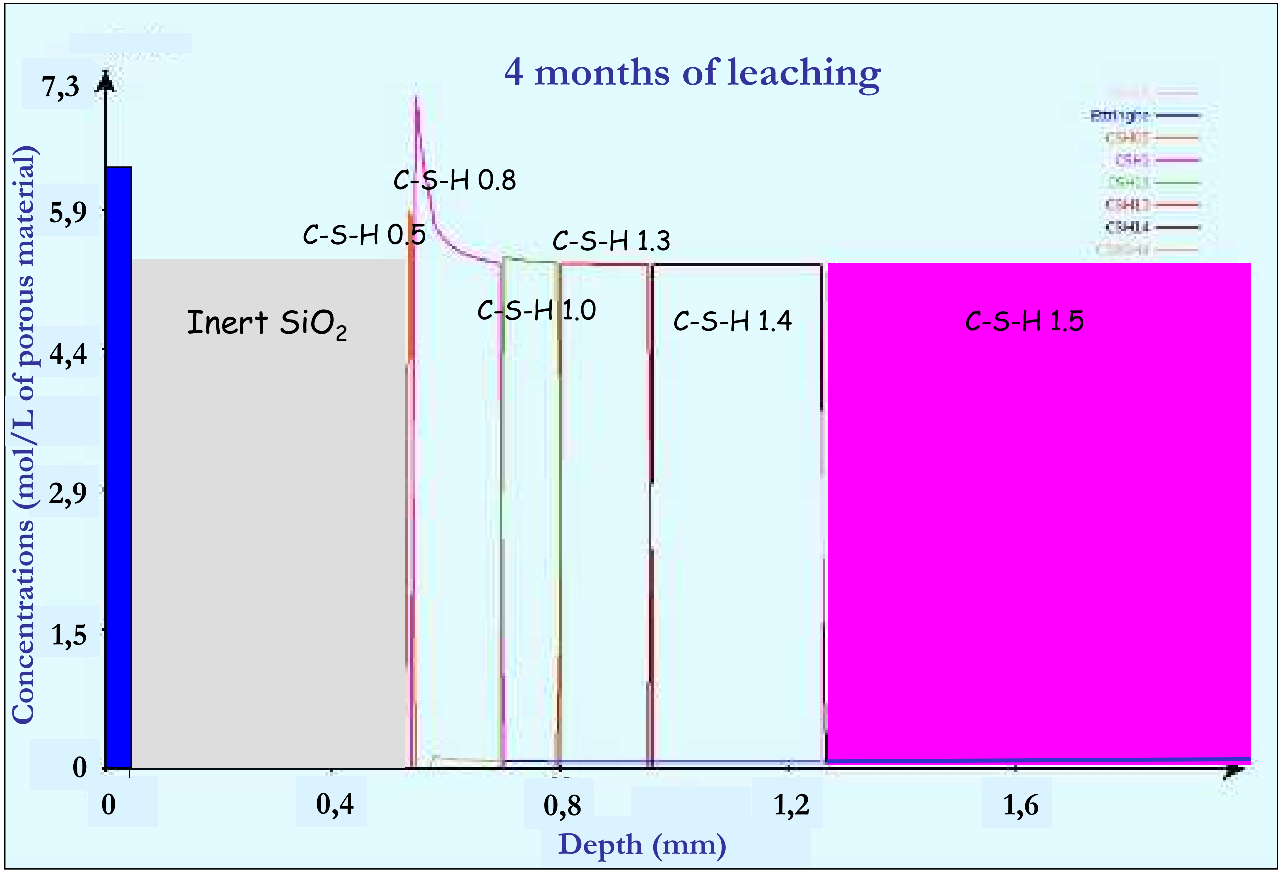
4. Durability of low-pH cement-based materials

Leaching at constant pH

Reactive transport model (HYTEC)

Cement paste B
(OPC 60% - SF 40%)

Sound core: ettringite +
C-S-H (C/S = 1.5)
Porosity : 35.4 %
$D_{app} = 5.10^{-12}$ m^2/s
$\alpha = 5$



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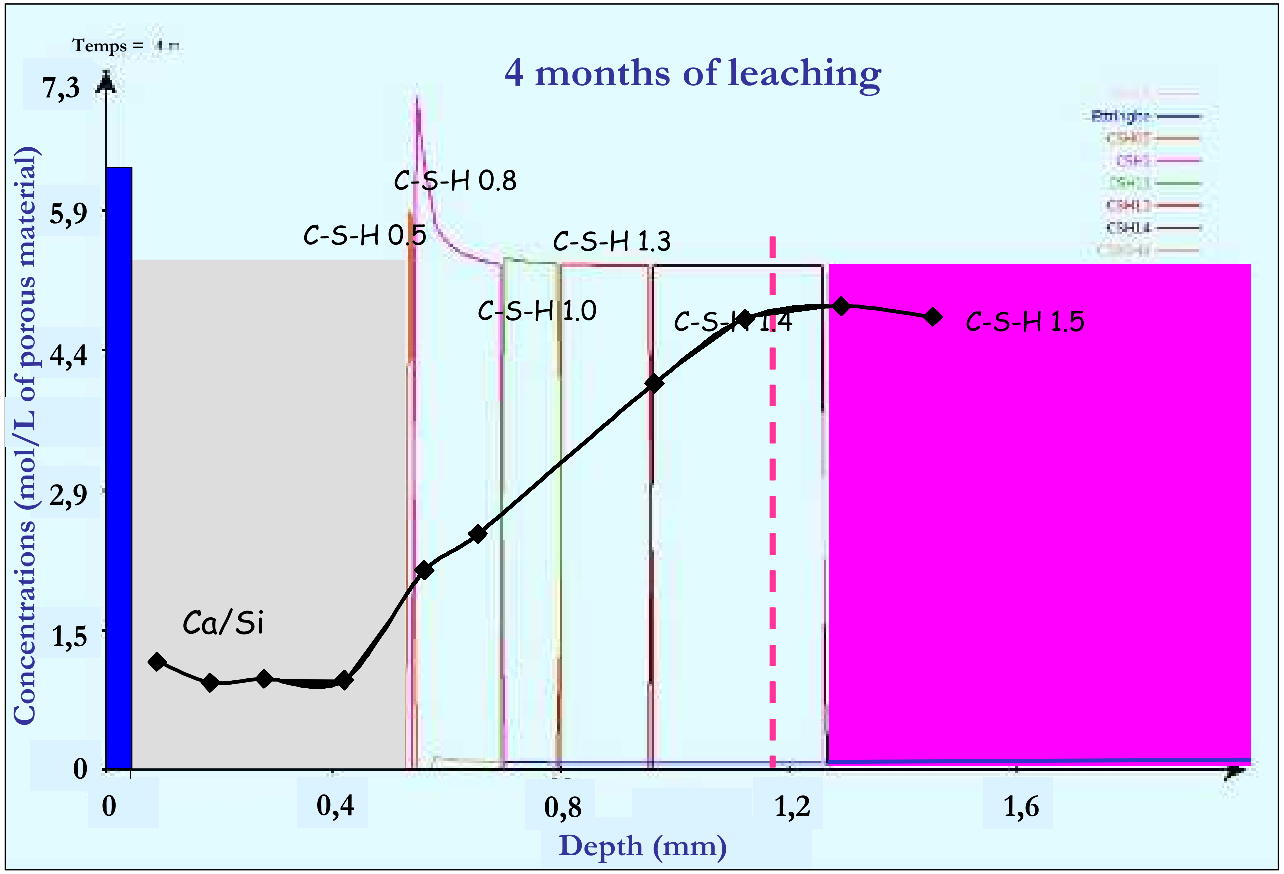


5. Field experiments

➢ **The TSX experiment** (funded by Canada, France, Japan, and USA)

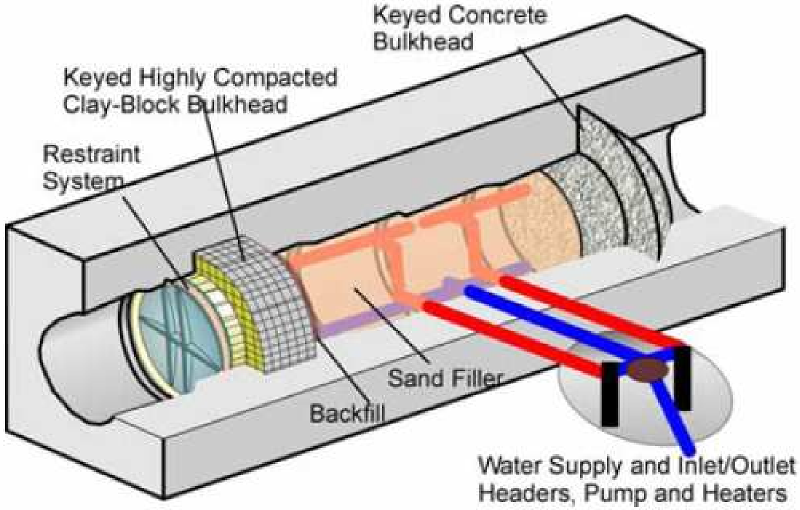
Canada 's URL, -420 m

Built from 1996 to 1998, decommissioned in 2004

↳ Full-sized concrete and clay bulkheads can be successfully constructed to effectively minimize any axial flow along a tunnel

(Chandler et al, 2002)

LHHPC concrete



➢ **POSIVA / SKB / NUMO** : Test of injection grouts for fractures with hydraulic apertures > 100 µm

- 2004: Helsinki multipurpose tunnel site
- 2005: Olkiluoto ONKALO access tunnel construction site

(Hansen et al., 2005)

Stabilization of deep core drilled boreholes

(Persson et al, 2005)

Preliminary test in a mock-up tunnel

➢ **JAEA: in situ shotcreting experiment planned at Honorobe URL in ≈2008**

Use of HFSC cement, preliminary tests completed - *(Kobayashi et al, 2007)*

5. Field experiments

ESDRED Project (Engineering Studies and Demonstration of Repository Design) – 2004 / 2009

- 13 organisations, 9 countries

  France: ANDRA, Spain: AITEMIN, CSIC, ENRESA, Germany: DBE TEC, GRS, Belgium: ESV EURIDICE GIE, ONDRAF/NIRAS, Switzerland: NAGRA, United Kingdom: NIREX, The Netherlands: NRG, Finland: POSIVA, Sweden: SKB

- Module 4: Temporary sealing technology (low pH cement & shotcrete)

Demonstration objectives:

- ✧ Develop a cement formulation which willl produce a concrete with a pH less than 11
- ✧ Use this concrete to develop a shotcrete formulation which can be used to construct low pH concrete plugs for retaining bentonite plugs as they expand
- ✧ Develop a low pH shotcrete formulation for rock support
- ✧ Construct a low pH plug underground and load it to failure
- ✧ Apply a skin of rock support shotcrete underground and monitor results

5. Field experiments

Module #4: Low pH Shotcrete Panels

ESDRED – Module 4

Major results to date (end 2007) :

➢ One meter long low pH plug constructed using shotcrete technique at Äspö

➢ Plug has been loaded to failure (sliding) and evaluation of results under way

MODULE # 4: Shotcrete Construction of Plug at Äspö HRL

➢ Skin of rock support shotcrete has been installed at Äspö and observation/monitoring is underway

http://www.esdred.info/

6. Conclusion

➢ Low pH cements can be designed from binary blends of OPC and SF with high SF contents (≈ 40%) or from ternary blends of OPC / SF / FA or BFS

➢ Properties of low-pH cement based materials, as compared to OPC references :

- ✧ bad workabillity counteracted by using increasing amounts of superplasticizers
- ✧ low heat of hydration
- ✧ higher porosity, but refined
- ✧ high mechanical strength
- ✧ higher dimensional instability
  significant shrinkage at early age
- ✧ pore solution pH ≈ 11 – strong reduction in the alkali content
- ✧ slower decalcification rate under leaching by pure water

➢ Despite the unusually high amount of pozzolanic additions in the blend, low pH shotcrete, injection grout or high strength concrete can be prepared using conventional engineering practices

6. Prospects

➢ **Cement chemistry**

✧ influence of temperature on the physico-chemical evolution of low-pH cements during hydration ?

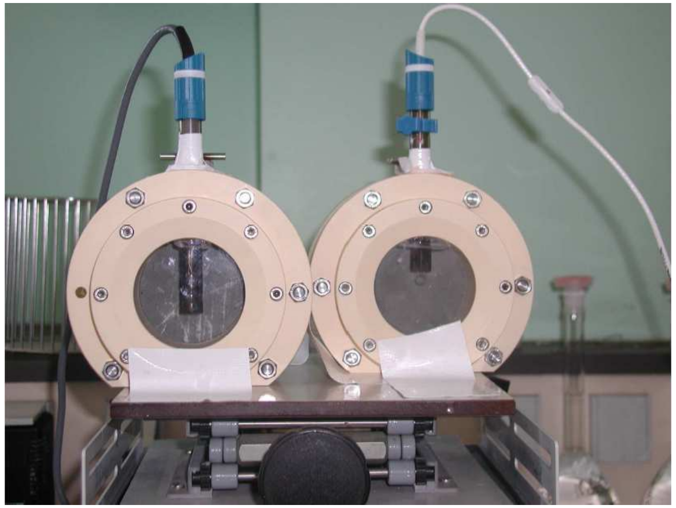
✧ need for a better understanding of the effect of the blending materials on the hydrated mineralogy and its development over time

✧ retention of alkalis by hydrated low-pH cement ?

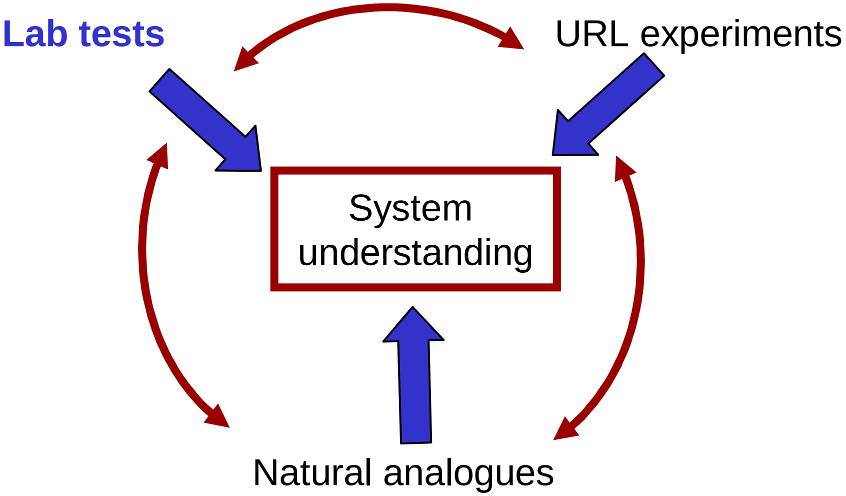
➢ **Modelling**

✧ Modelling of leaching has to be improved
- lack of data for diffusion coefficients
- need for a better assessment of the proportion of reacting blending material

➢ **Interaction with bentonite**



(Dauzères, 2008)



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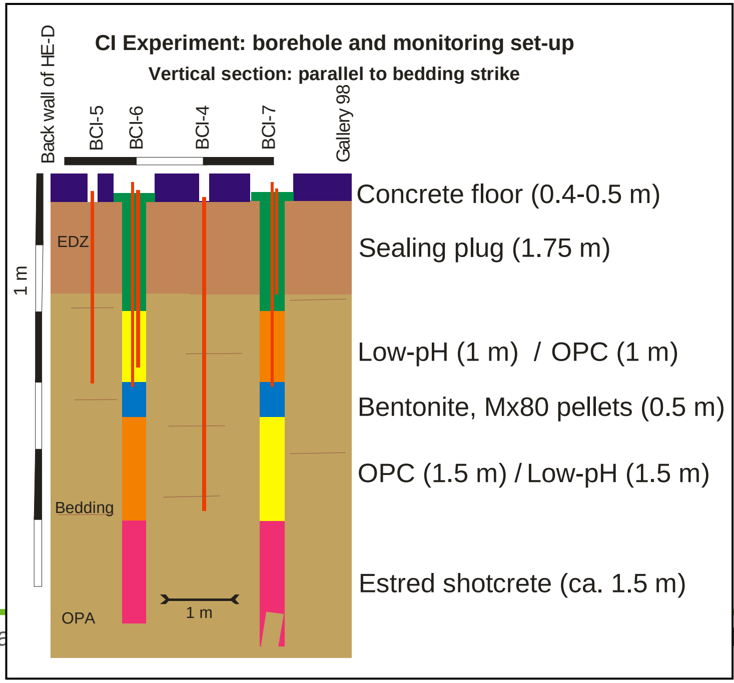
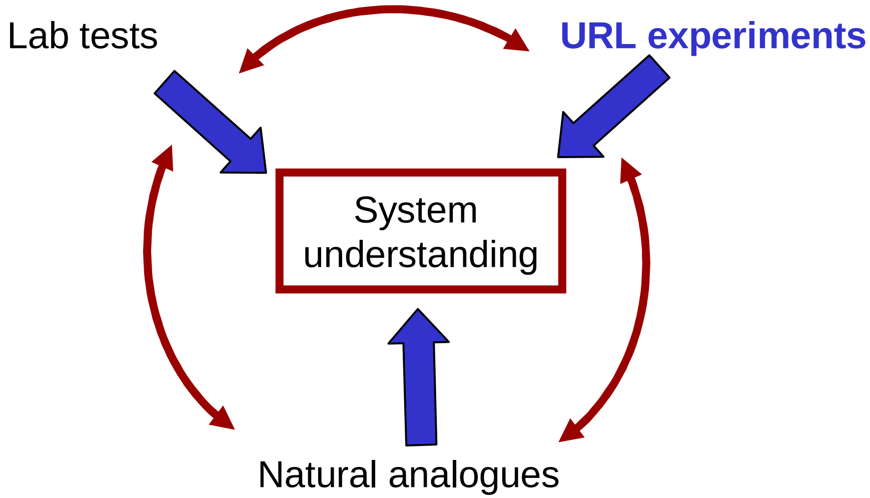
CI experiment, Mont Terri



(Berner, 2008)



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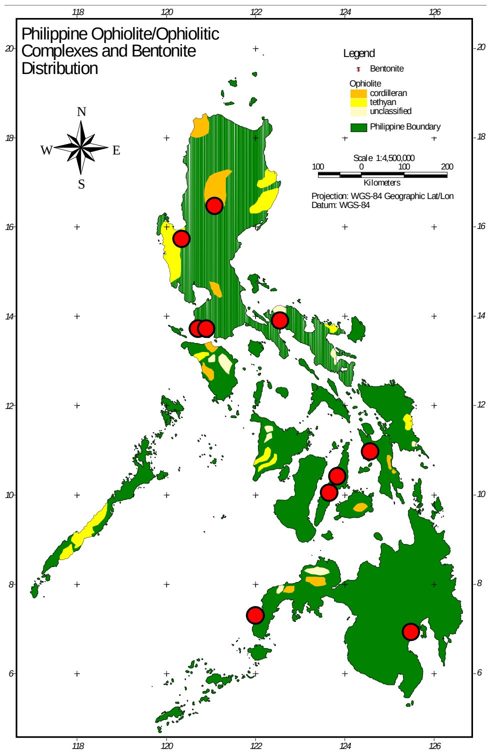
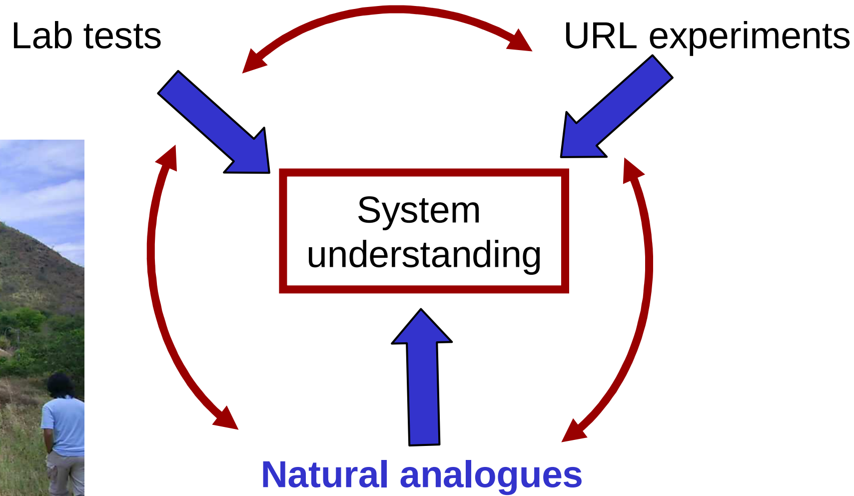


Mangatarem site



(Alexander, 2008)

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and…

Thank you for your attention !