MECHANISMS AND MODELLING OF WASTE/CEMENT INTERACTIONS
2nd International Workshop

Low pH concrete resistance against underground water aggression

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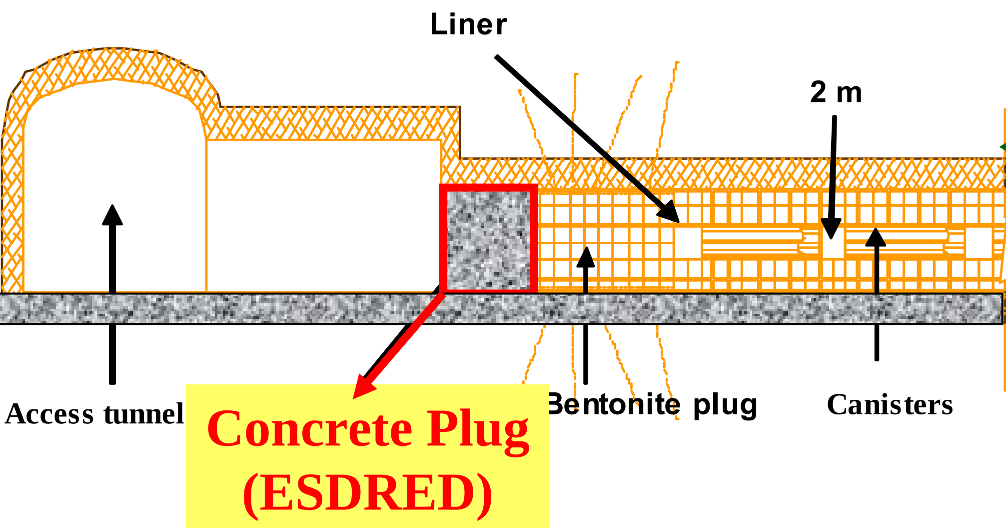
SCOPE

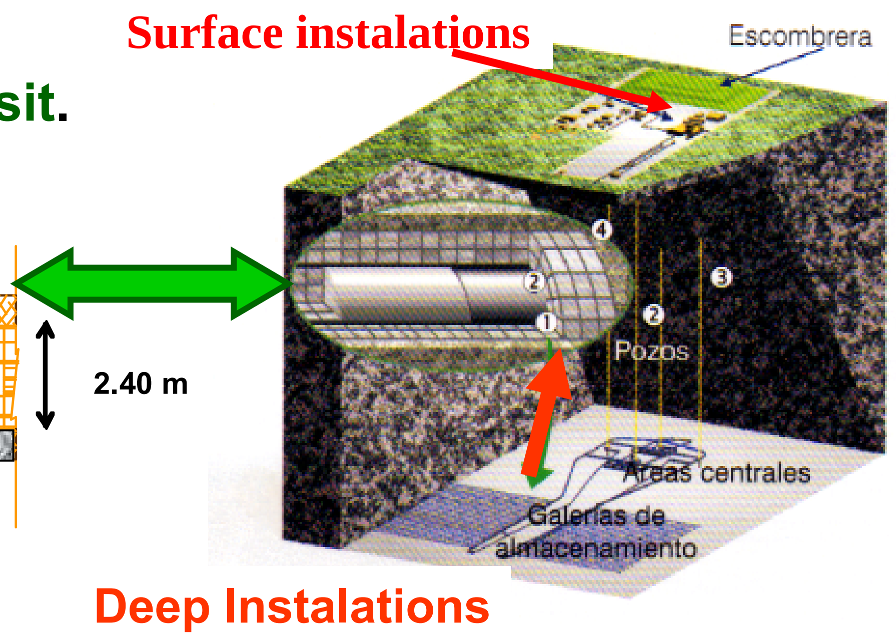
- **Design of low-pH cements for underground repositories of HLRW**
- **Microstructure evolution of low-pH cement pastes**
  - **OPC based**
  - **CAC based**
- **Resistance of low-pH cementitious materials to underground waters aggression**

Design of low-pH cements for underground repositories of HLRW

Role of Cementitious Materials in Deep HLRW

10000 Concrete Tons Granitic Reposit.





Structural cast concrete: road paving, floors or operational structures.

Shotcrete: either for tunnels linings, rock support or for plug tunnels

Rock bolts

Grouting: to inject fractures, for sealing

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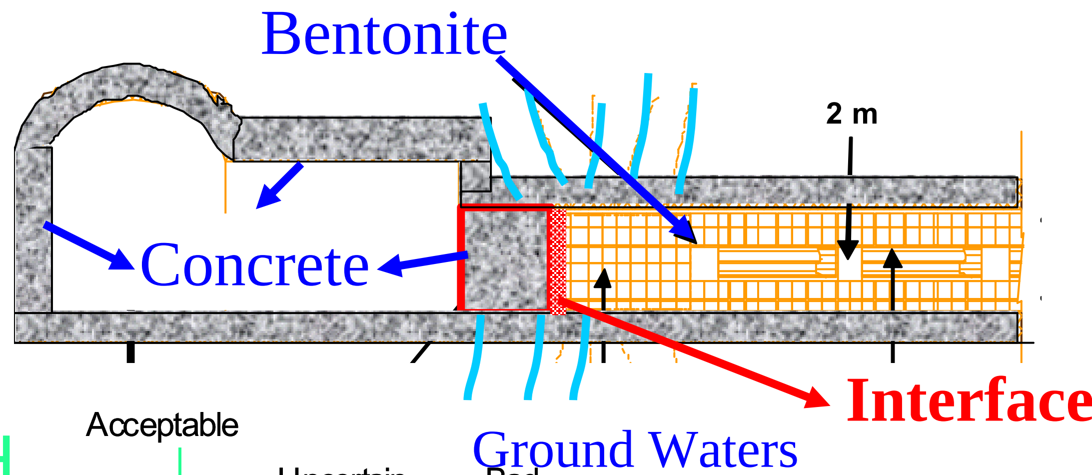
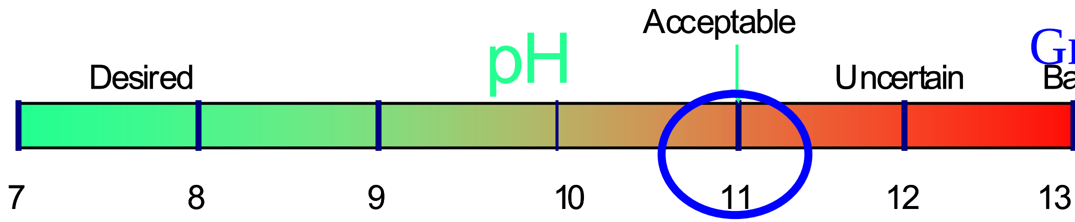
Need of Low-pH Cements for HLRW Repositories

Interaction of concrete with ground waters liberates "Hyper-alkaline plume" pH>12.6 perturbs the integrity of Bentonite barrier





The risk corrosion alteration of bentonite barrier is higher if pH >>11

USE LOW pH CONCRETE ⇒ LOW-pH CEMENT

REQUIREMENT: Pore water pH ≤11

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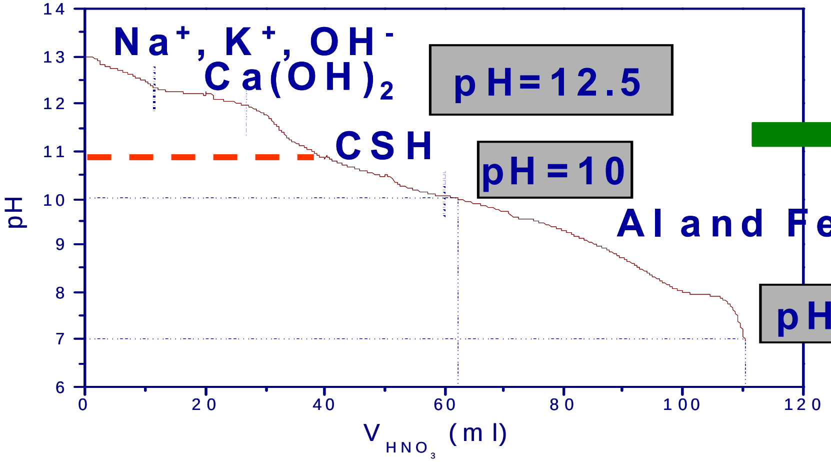
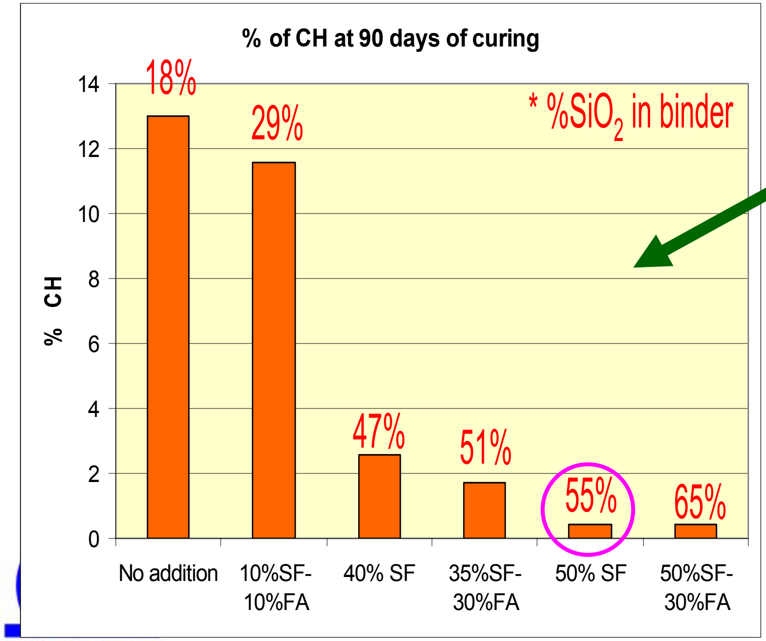
Criteria for designing low-pH cements from OPC



Alkaline plume origin

Cement components responsible for high alkaline pH of pore water: Na^+, K^+ and Portlandite ($Ca(OH)_2$)

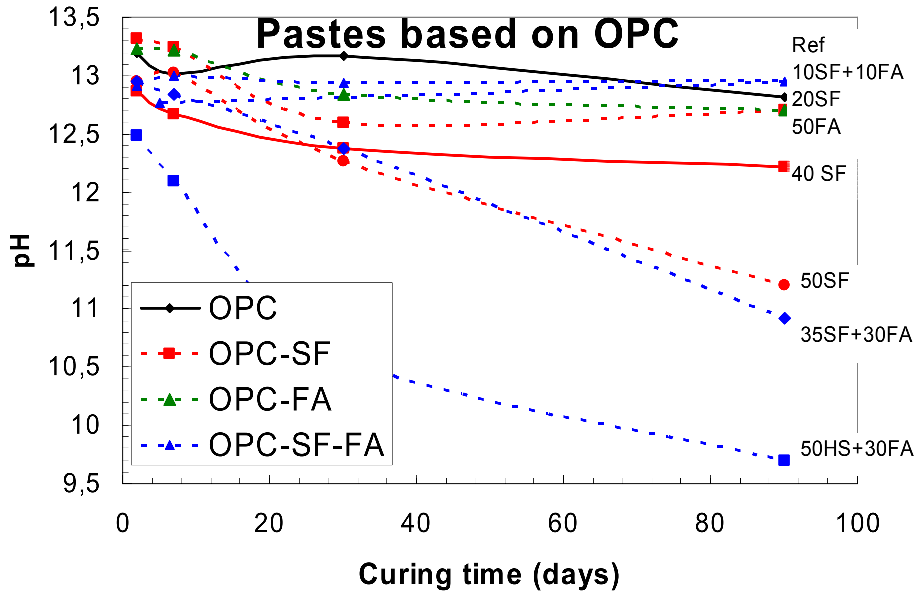
Elimination of OH^- sources Portlandite Crystals



Pozzolanic Reaction

$Ca(OH)_2$ + Mineral Admix.

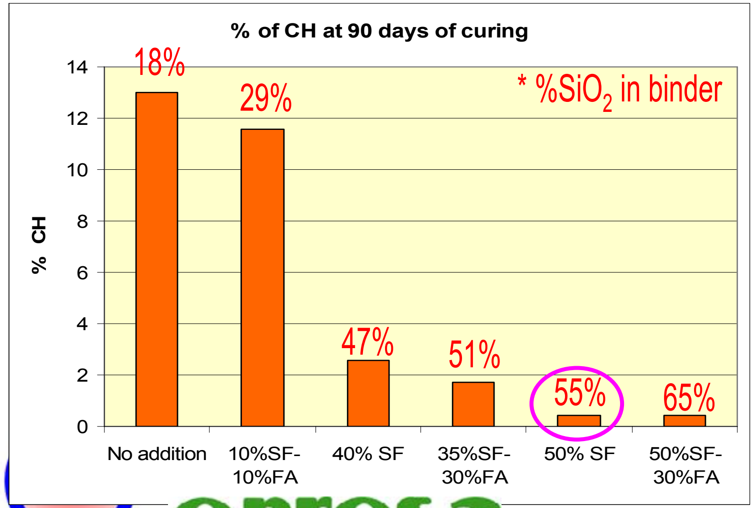
Criteria for designing low-pH cements from OPC

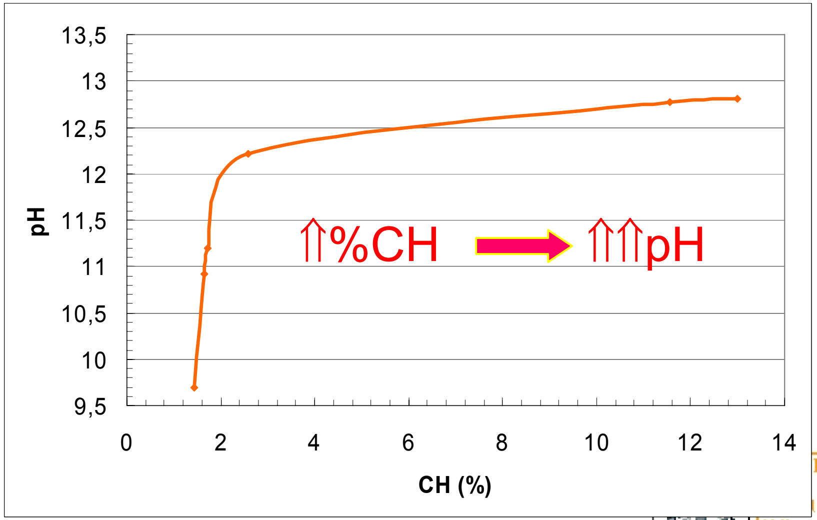


SF is very efficient ↓ pH

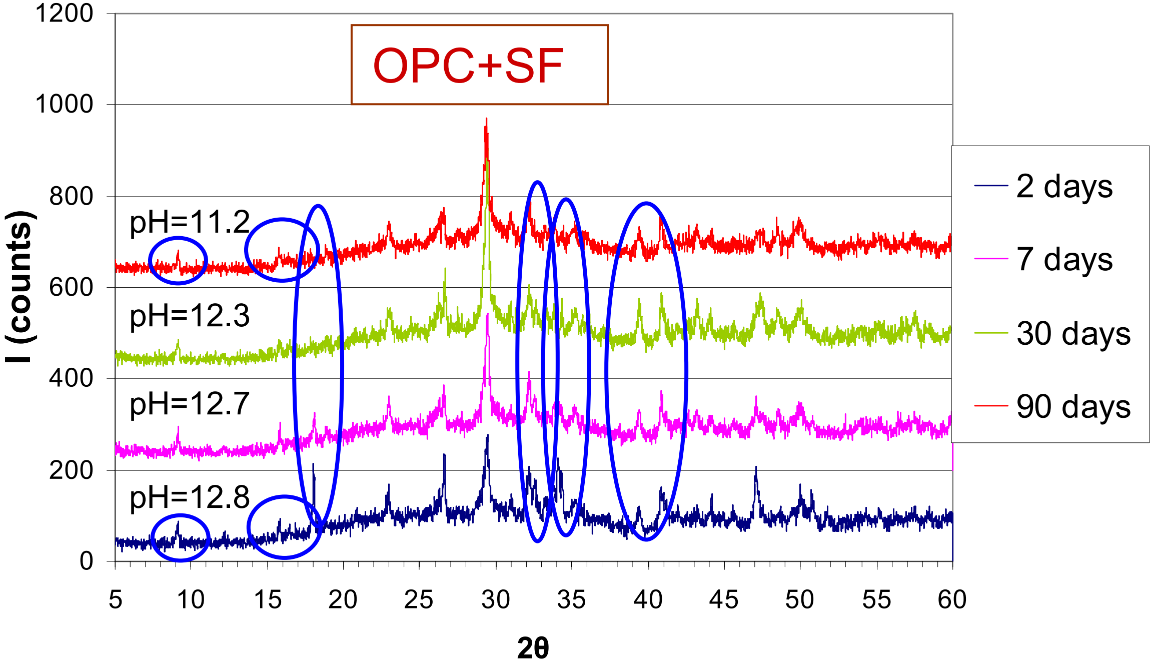
SF>>>FA

↑%MA ➡ ↓pH





Microstructure evolution of low-pH cement pastes – OPC based

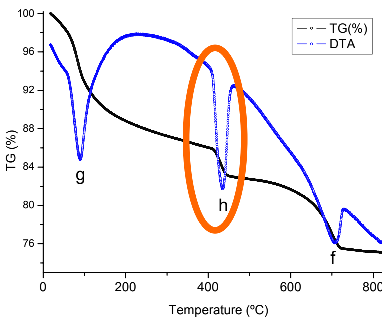


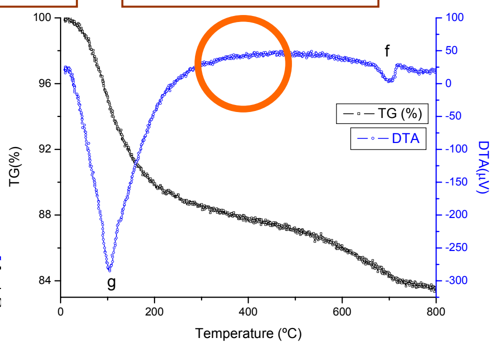
-Dissaprearance of CH

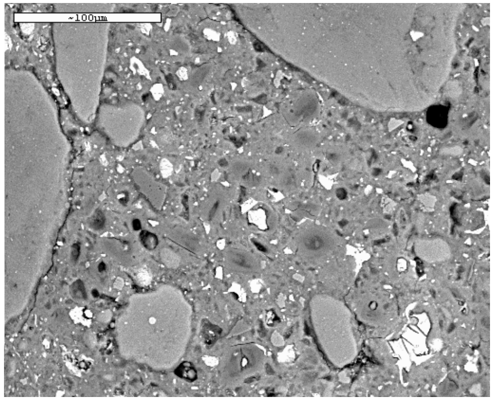
- C_2S and C_3S

- ettringite

OPC | 90 d | OPC+SF







- No micro cracks.
- Good texture.
- Anhydrous grains of SF
- C/S ratios of the CSH gel between 1-0.7
- Anhydrous cement

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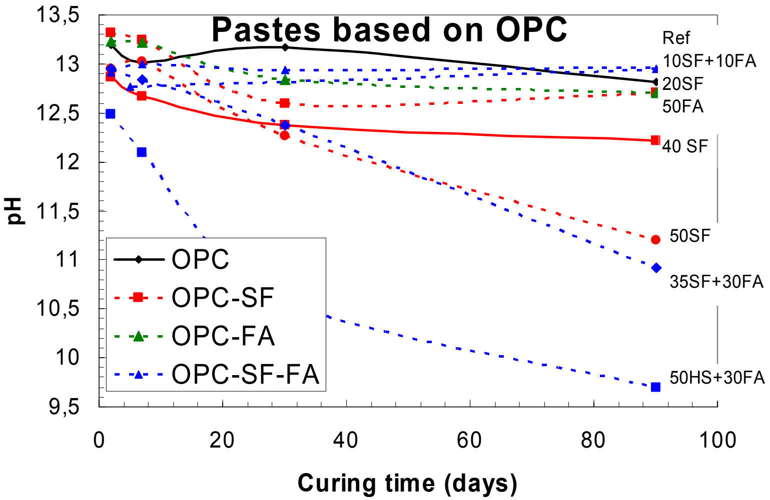
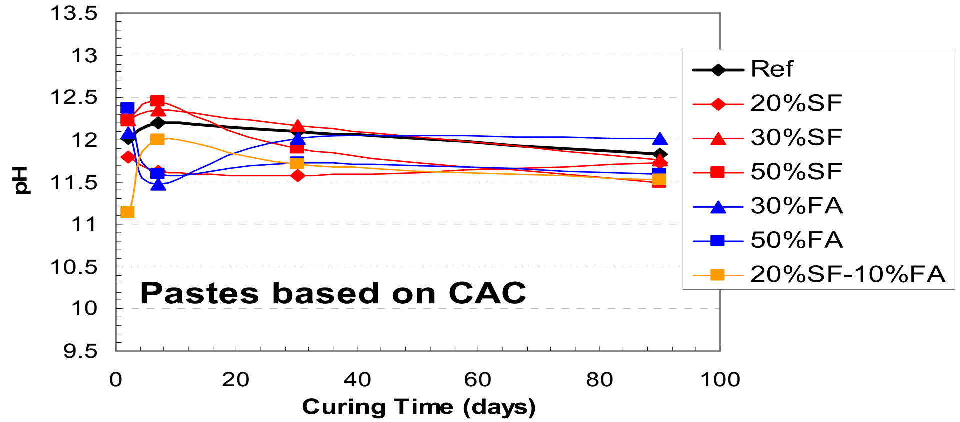
Criteria for designing low-pH cements from CAC



1st.- CAC achieves an acceptable pore fluid pH



90 days: pHs < 12.

MA do not significantly ↓pH (50% MA ↓pH in 0.5 points)

2^{nd}.- Conversion Process:

$$3\,CAH_{10} \rightarrow C_3AH_6 + 2\,AH_3 + 18\,H$$

$$3\,C_2AH_8 \rightarrow 2\,C_3AH_6 + AH_3 + 9\,H$$

↑ Porosity→ ↓ compressive strength

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Microstructure evolution of low-pH cement pastes – CAC based

Short Ages (< 7d)

CAC and CAC+SF

CAH_{10}

C_2AH_8

AH_3

Long Ages (>30d)

CAC

AH_3

C_3AH_6

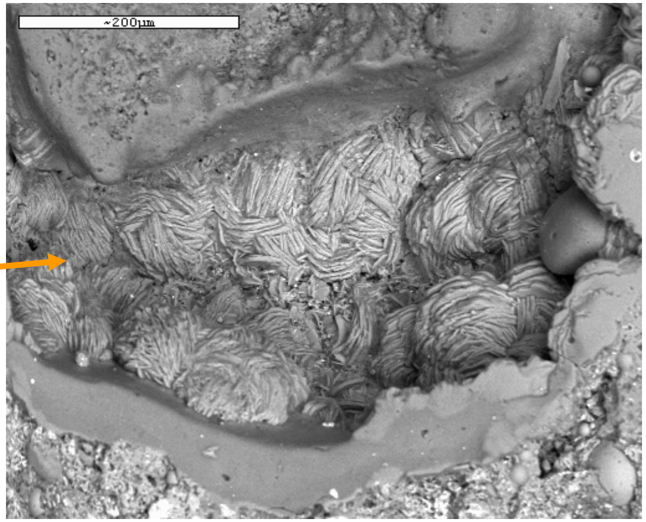
CAC + SF

alumina gel

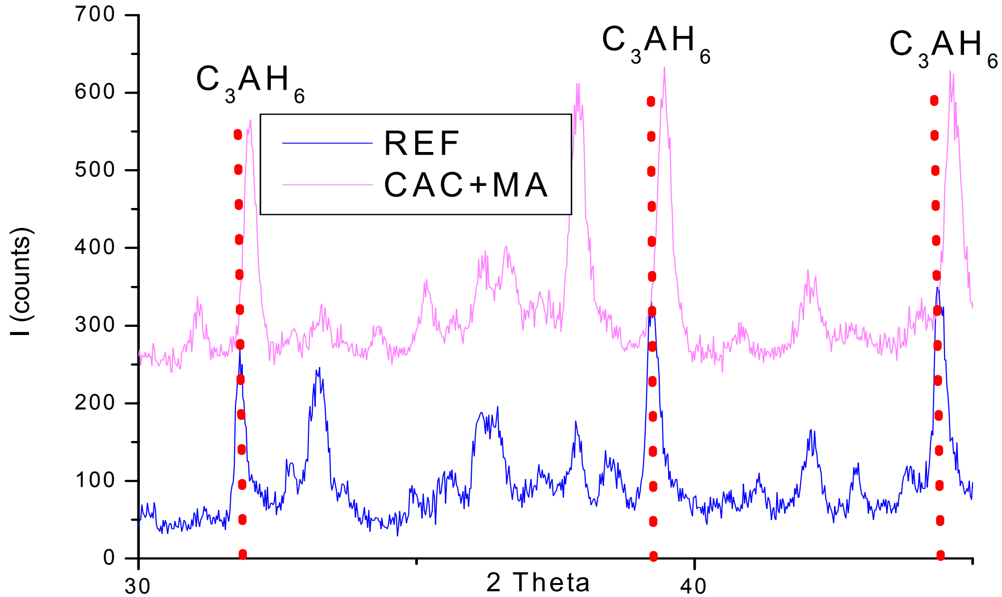
AH_3

C_2ASH_8

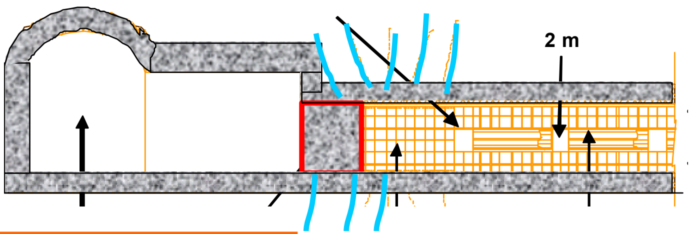
$C_3AS_{3-X}H_{2X}$



BSEM confirms the existence of hexagonal platelets of gehlenite



Resistance of Low-pH concretes to water aggression: Percolation test



Concrete + ground waters

leaching of pore solution

alteration of the solid phases

loss of concrete properties

Although the degradation rate is very slow its evaluation is important for structures near field RWR, where extremely long-term stability is needed. In laboratory accelerated tests are used to qualify the different concretes for deep repositories

Cement degradation depends on: composition, porosity, density, leachant characteristics, flow rate, Tª and water chemical composition

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Interaction of low-pH concretes with ground waters

Basic concretes samples

70%CAC+30%SF

60%OPC+40%SF

Constituents	Kg/m³
Water (kg/m³)	128
Binder (kg/m³)	320
Water/binder	0.4
Fine Gravel (4-8 cm) (kg/m³)	855
Sand (0-4 cm) (kg/m³)	1033
Superplasticizer (kg/m³)	3.2

Constituents	Kg/m³
Water (kg/m³)	160
Binder (kg/m³)	320
Water/binder	0.5
Fine Gravel (4-8 cm) (kg/m³)	855
Sand (0-4 cm) (kg/m³)	1033
Superplasticizer (kg/m³)	3.2

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Interaction of low-pH concretes with ground waters

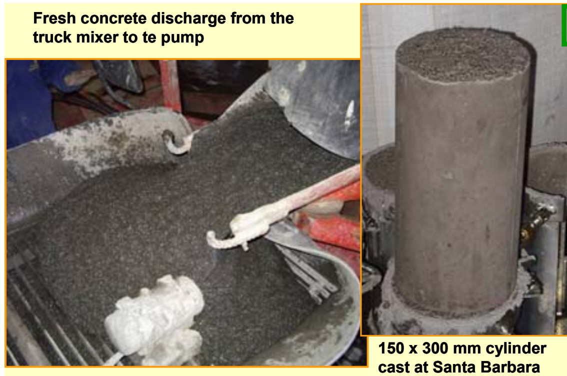
Cores from shotcreted concrete (Äspö)

60%OPC+40%SF

Low pH cement formulations

Compatibility with chemical admixtures

Low pH basic concrete design



Constituents	Kg/m³
Water (kg/m³)	277.2
Binder (kg/m³)	307.2
Water/binder	0.9
Coarse Aggregate (8-12 mm) (kg/m³)	615.6
Medium Aggregate (4-8 mm) (kg/m³)	199.7
Sand (0-4 mm) (kg/m³)	818.1
Superplasticizer (kg/m³)	5.5
Accelerator (kg/m³)	18.5

Shotcreting

Shotcreted plug

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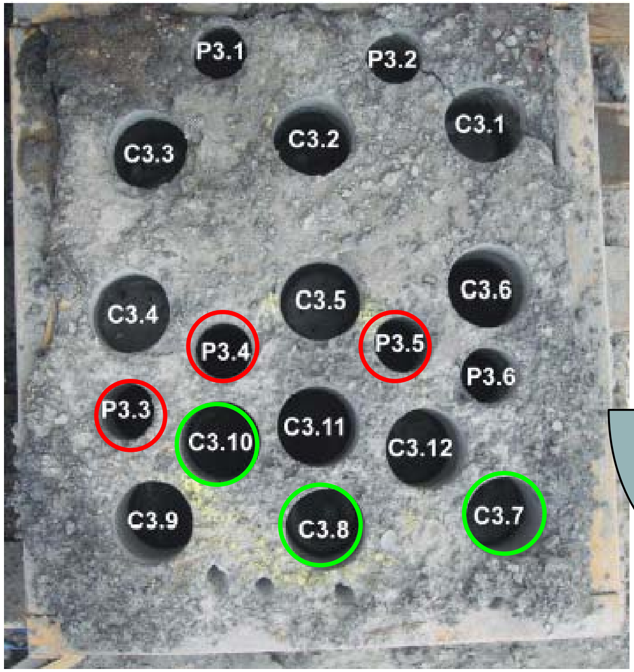
Interaction of low-pH concretes with ground waters

Cores from shotcreted concrete (Äspö)

60%OPC+40%SF

Extraction of cores for testing



Core

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Interaction of low-pH concretes with ground waters

Percolation Test (accelerated)

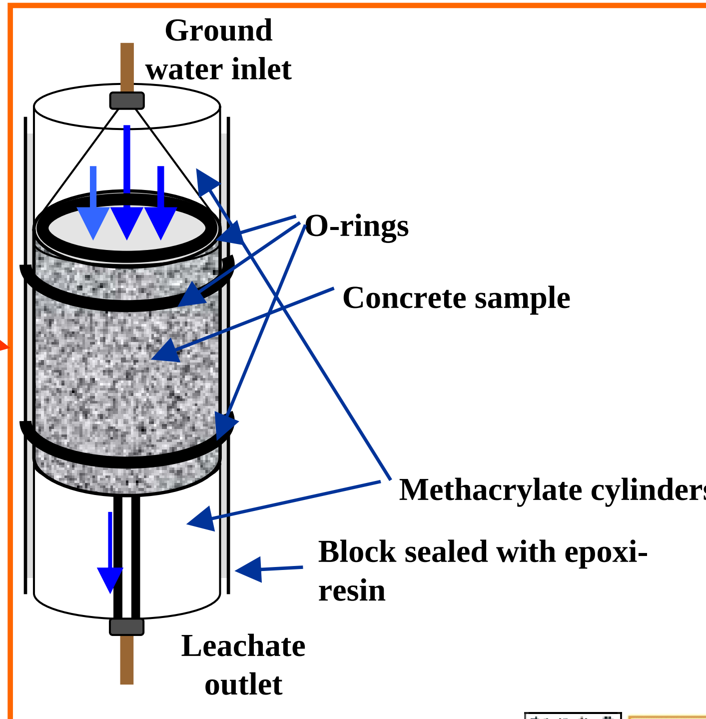
Ground water composition from Äspö

	Cl^-	SO_4^{2-}	NO_2^- or NO_3^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	Si^{4+}	pH
[ppm]	2681	225	-	1129	9.36	355	5.75	7.50	8.20

Air inlet for achieving the defined pressure value (0.5 bars)

Concrete or shotcrete plug samples

Leached solution



Column leaching test (open system).
Unidirectional flow.
Control of the inflow and outflow solutions.
Samples are saturated for 24 hours.

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Interaction of low-pH concretes with ground waters

Parameter Tested

Test time: low-pH concretes: 14 months; low-pH shotcrete : 2 years

leachate

- Leachate flow rate

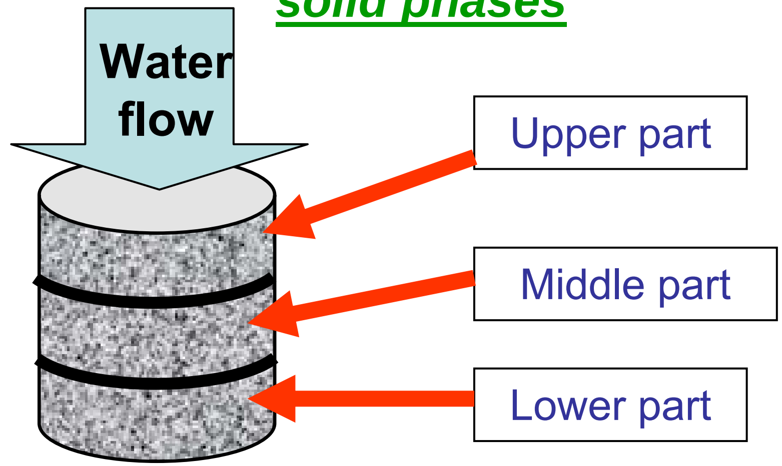
Hydraulic conductivity

Variations
Requirement (≈$1x10^{-10}$ m/s)

- Leachate pH
- Chemical composition

Measure continuously during test

solid phases



Techniques used in each sample part

- Back Scattering with EDAX analyses
- Optical microscopy (Carbonation test)
- Mercury Intrusion Porosimetry
- DRX
- ATD/TG
- RMN

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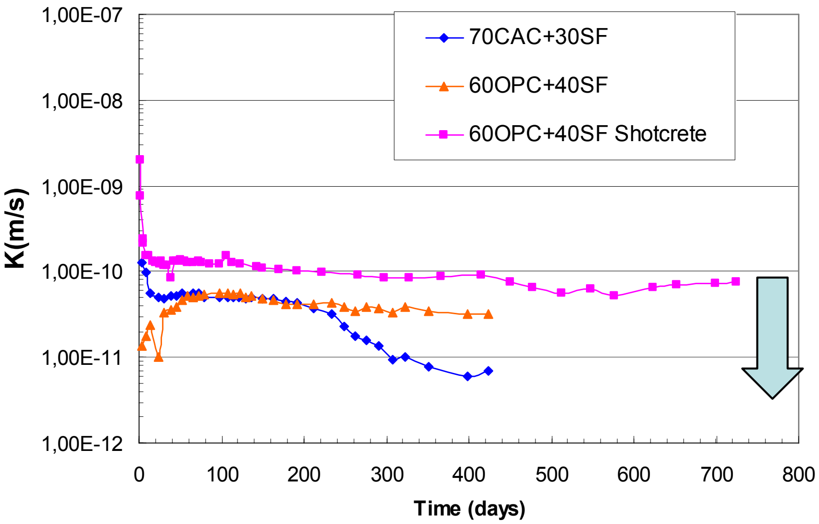
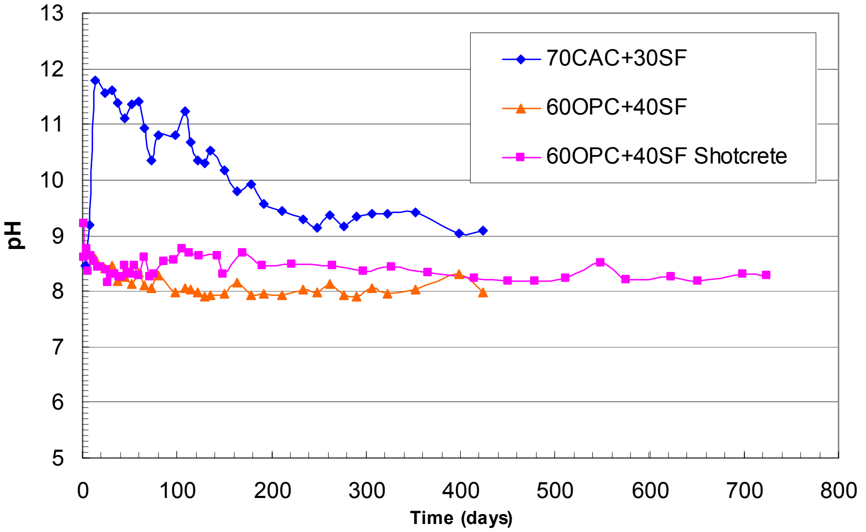
Interaction of low-pH concretes with ground waters

Leachate results

Hydraulic conductivity evolution



pH evolution



Hydraulic conductivity (HC) ≅ $1x10^{-10}$ m/s Concretes < shotcrete

OPC: pH leachate becomes stable soon (pH≤9)

CAC: pH decreases slowly, ranges 12→9

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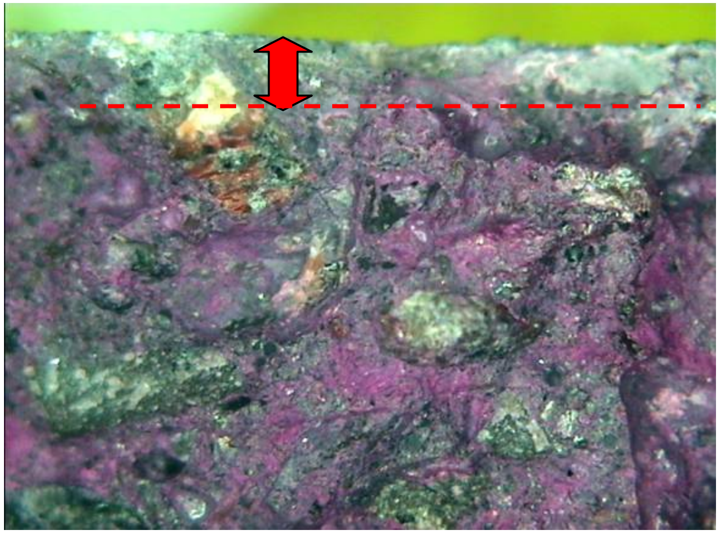
Interaction of low-pH concretes with ground waters

Optical microscopy- phenolphtaleine test

Estimation of the altered front

70%CAC+30%SF

60%OPC+40%SF



A small altered front can be seen with both types of cement

CAC based	OPC based
650µm ± 100µm	700µm ± 130µm

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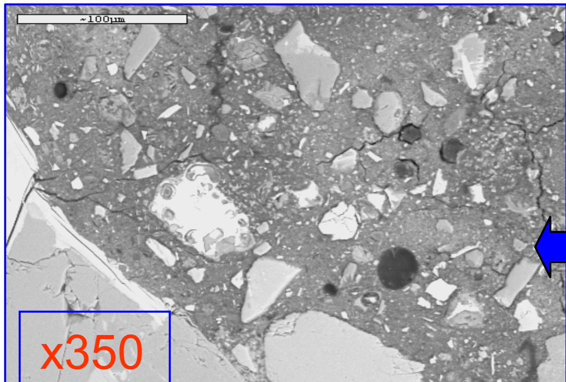
Interaction of low-pH concretes with ground waters

BSEM

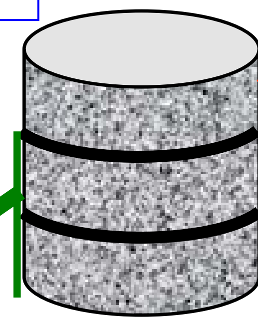
60%OPC+40%SF

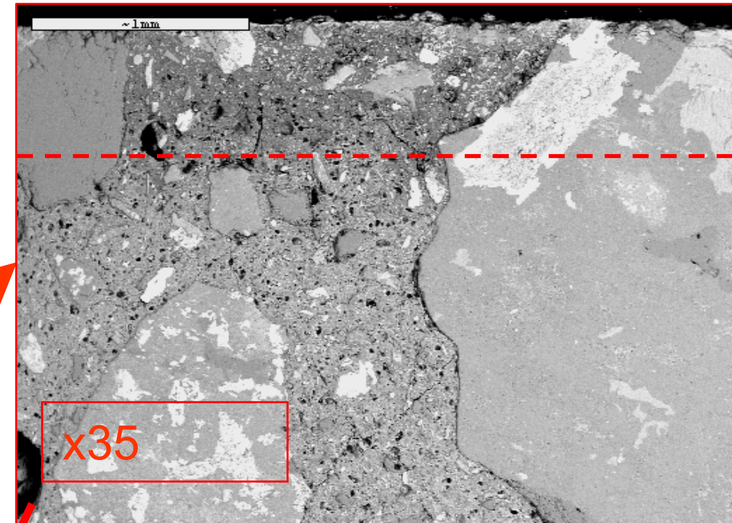
shotcreted concrete



Initial low-pH sample

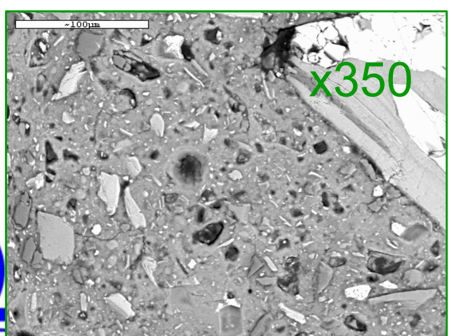
- Good aggregate-paste interfaces.
- Presence of anhydrous phases.
- CSH: $CaO/SiO_2 \approx 0.65\text{-}0.7$

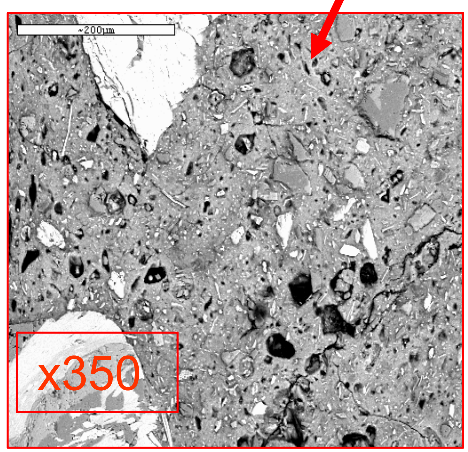


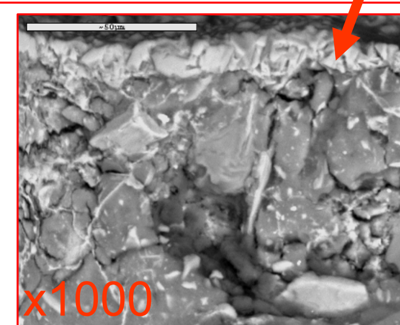


- Porosity increases
- ⇓ Anhydrous cement grains
- CaO/SiO_2 similar to ref.
- Good agg-paste interfaces.
- Densification in lower part
- No ⇑ microcracks

- Porosity increases
- ⇓ Anhydrous cement grains
- ⇓ CaO/SiO
- Good agg.-paste interfaces
- No ⇑ microcracks
- Calcite precipitation in surface
- Rich Mg solid phases







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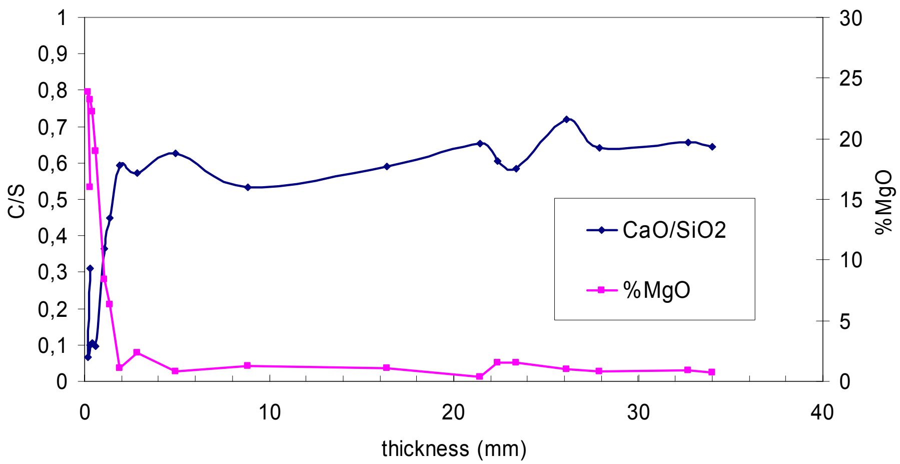
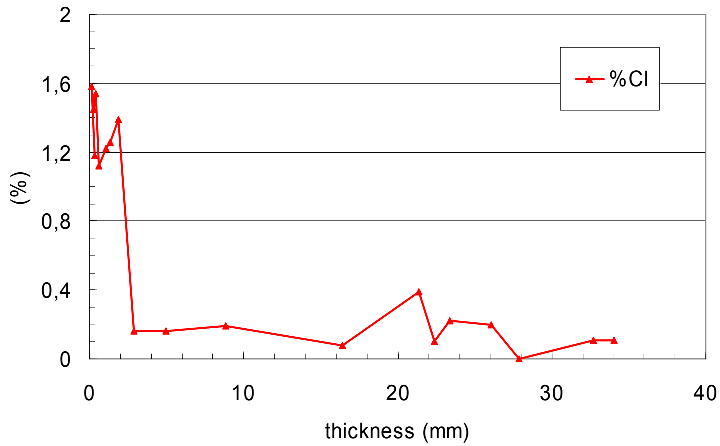
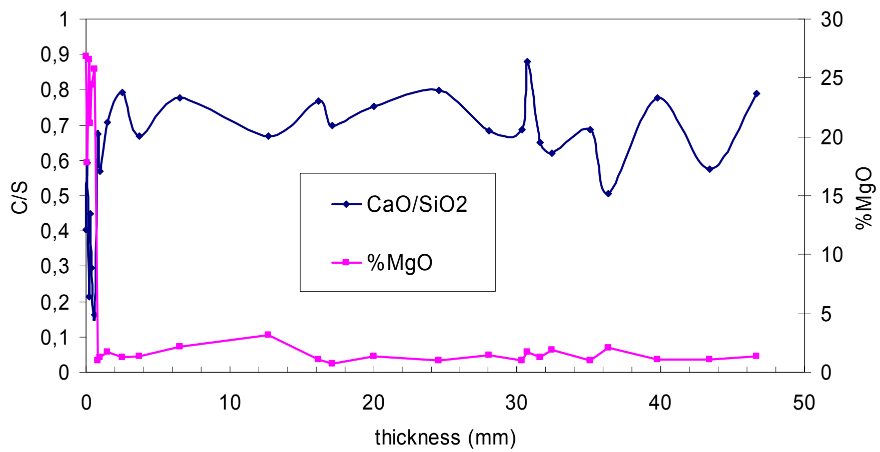
Interaction of low-pH concretes with ground waters

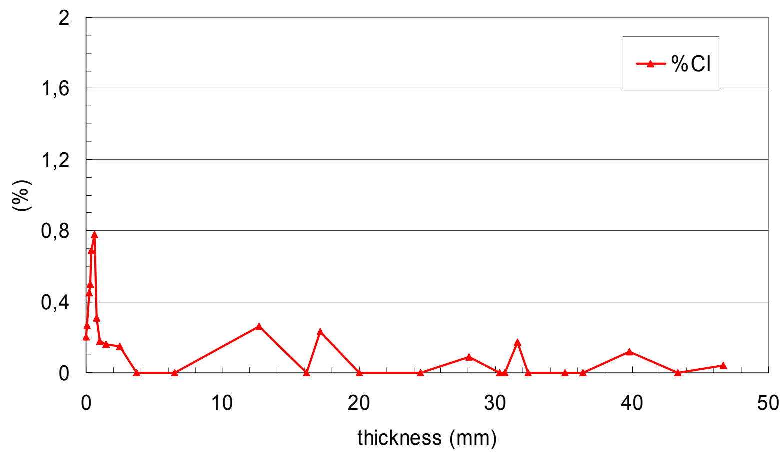
60%OPC+40%SF-shotcreted concrete- EDX Profiles





60%OPC+40%SF EDX Profiles





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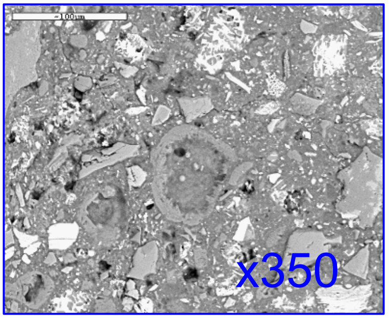
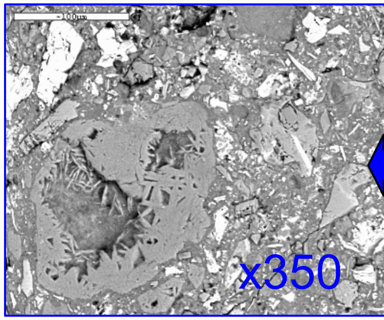
Interaction of low-pH concretes with ground waters

BSEM

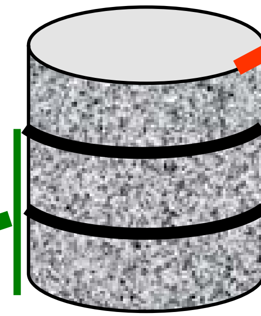
70%CAC+30%SF



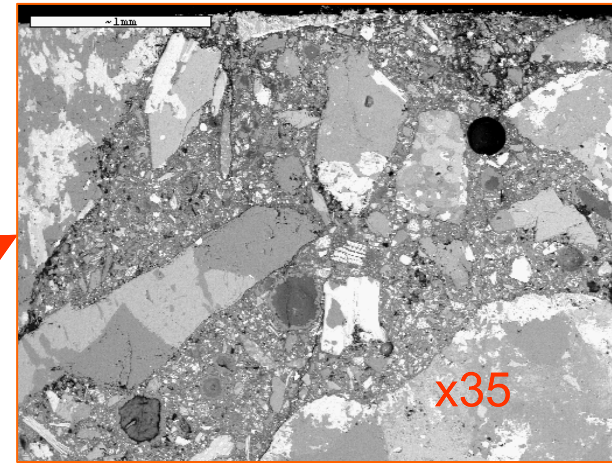


Initial CAC+SF concrete

- Good aggregate-paste interfaces.
- Presence of anhydrous phases.
- Paste composed of CASH
- Platelets of gehlenite.

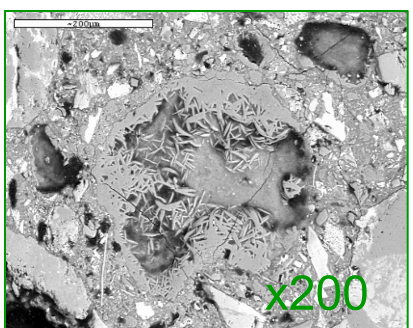


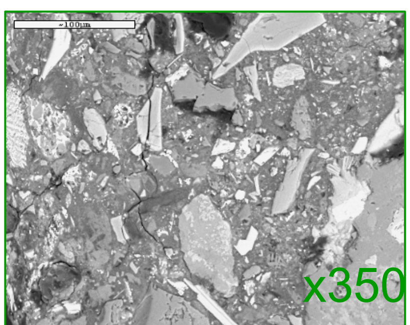
Control of Hydrate conversion

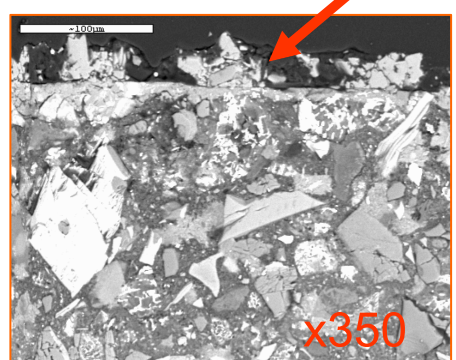


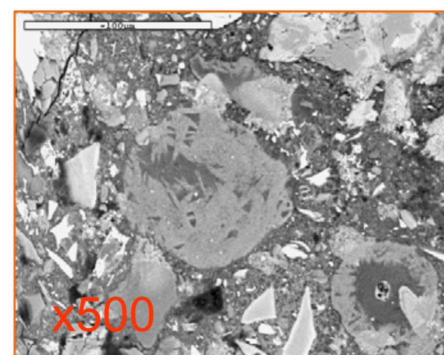
- ⇓ Anhydrous phases
- Paste composed of CASH
- ⇑ gehlenite platelets
- Good agg-paste interfaces
- No ⇑ microcracks
- Calcite precipitation

- ⇓ Anhydrous phases
- Paste composed of CASH
- ⇑ gehlenite platelets
- Good agg-paste interfaces
- No ⇑ microcracks





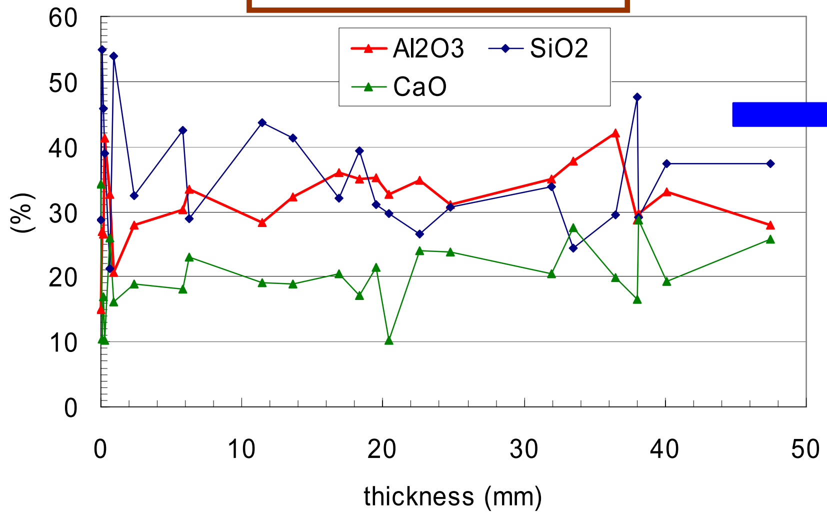




Interaction of low-pH concretes with ground waters

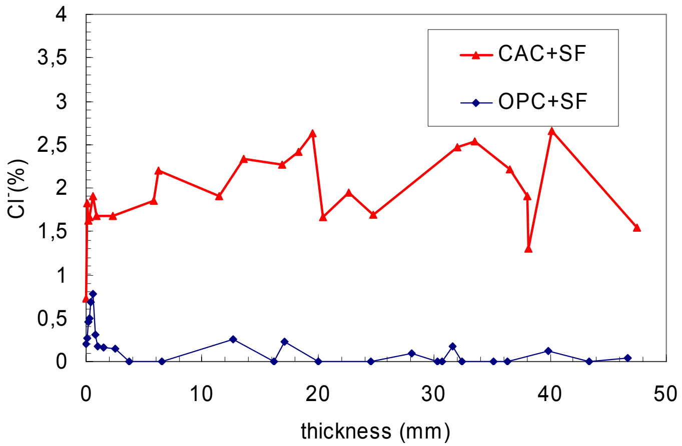
70%CAC+30%SF EDX Profiles

After 14 months



CASH analyses similar to initial state

%Cl- CAC based > %Cl- OPC based



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Preliminary Conclusions

1. The development of low-pH cement formulations implies the use of MA with high silica content, both for materials based on OPC and on CAC, in the first case for decreasing the pore fluid pH and in the second case for controlling the conversion process.

2. Microstructure of low-pH cement pastes based on OPC shows a dense paste based on a CSH matrix with C/S ratio = 1-0.7

3. Microstructure of low pH cement pastes based on CAC also presents a dense aspect and it is mainly based on a CASH matrix.

4. Preliminary results of percolation tests show a good resistance of the fabricated low-pH concretes against ground water aggression, although an altered front is observed from the surface in all the tested samples. Tested samples show a good HC and pH leachate value during all the test time.

Thank you for your attention