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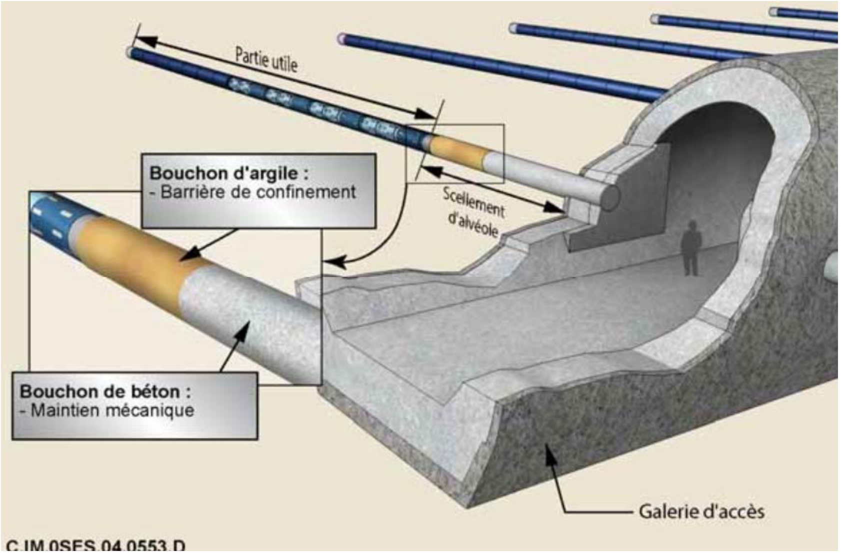
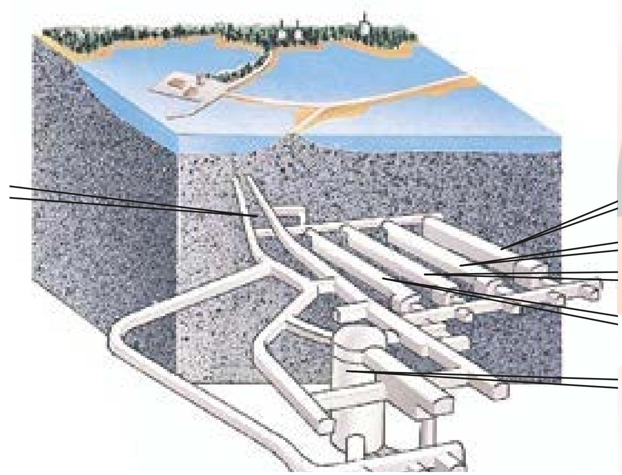
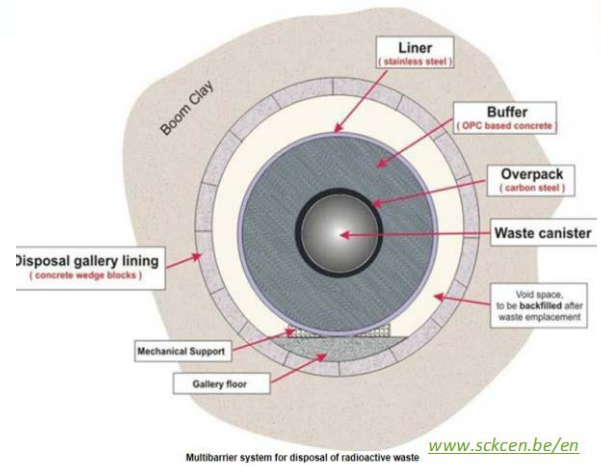
SCIENTIFIC AND STRATEGIC ENVIRONMENTAL CONSULTING

Modelling systems driven by the presence of cement

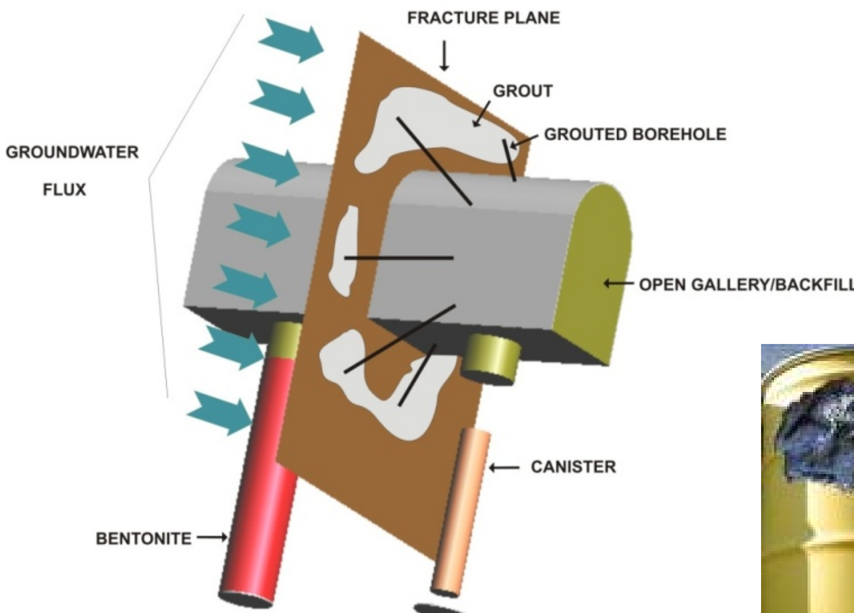
L. Duro, M. Grivé, J. Molinero, F. Grandia







Ubiquity of Cement materials



Need to understand and quantify effect of cementitious materials

- The cement system, its evolution and modelling approaches
  - Changes in chemistry of waters: pH/Eh/Ca content
  - Interfaces: changes induced in other materials properties
  - Cement alteration:
    - porosity, permeability changes
    - Release of other components: additives, organics
    - …
- RN chemistry in the presence of cement
  - Speciation
  - Solubility
  - Sorption

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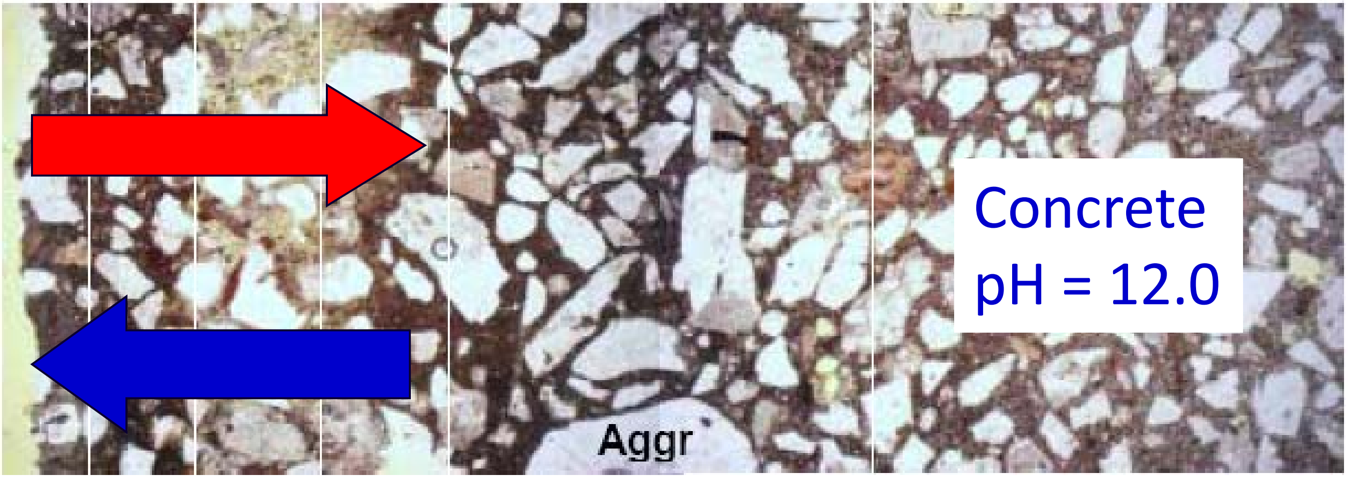
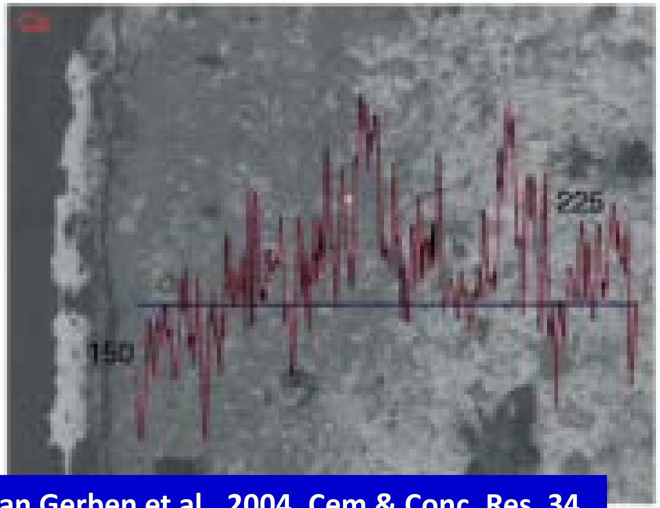
>The concept…

Groundwater
pH = 7.0

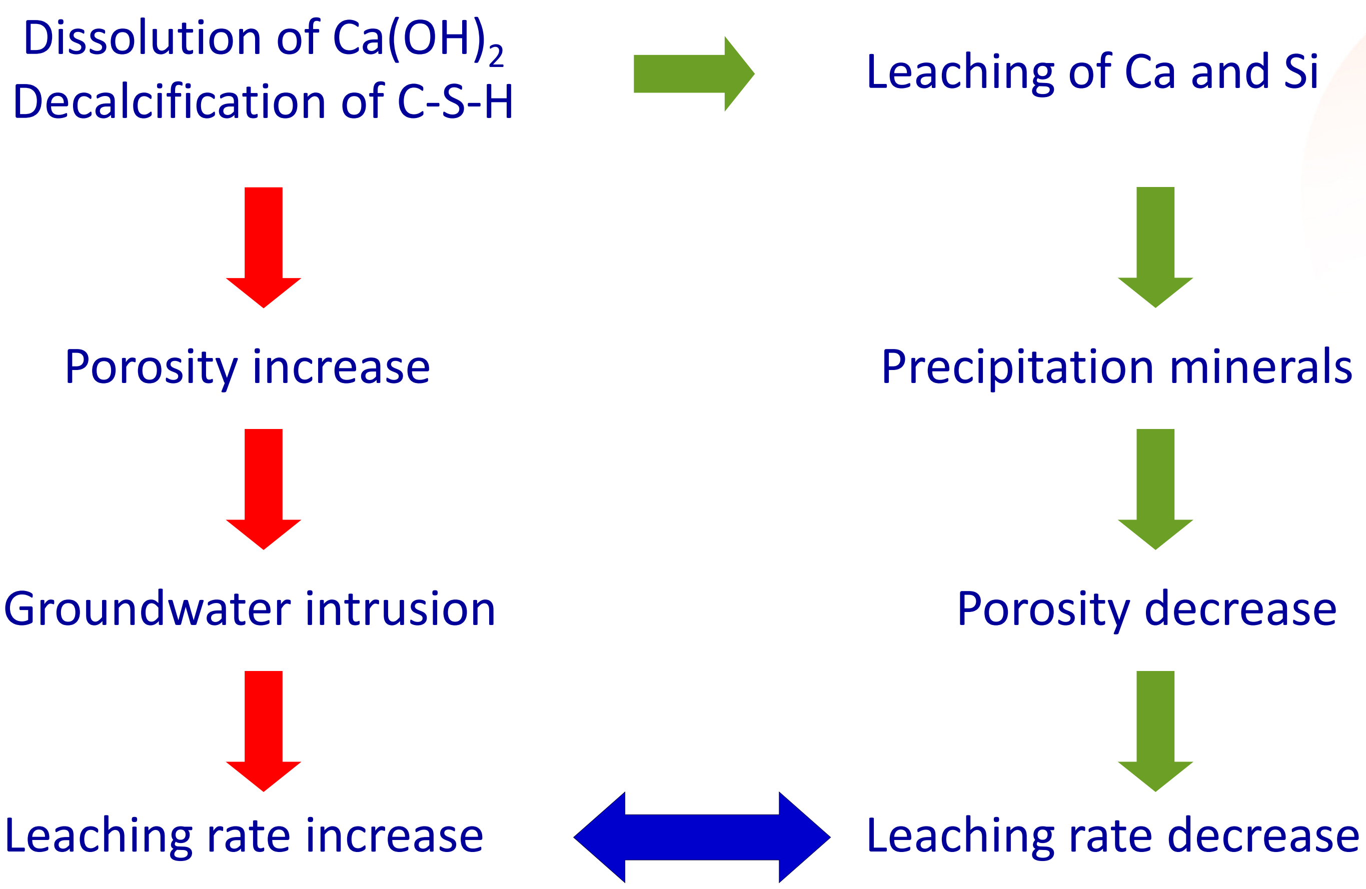


Leaching process



Van Gerben et al., 2004. Cem & Conc. Res. 34

>The concept…



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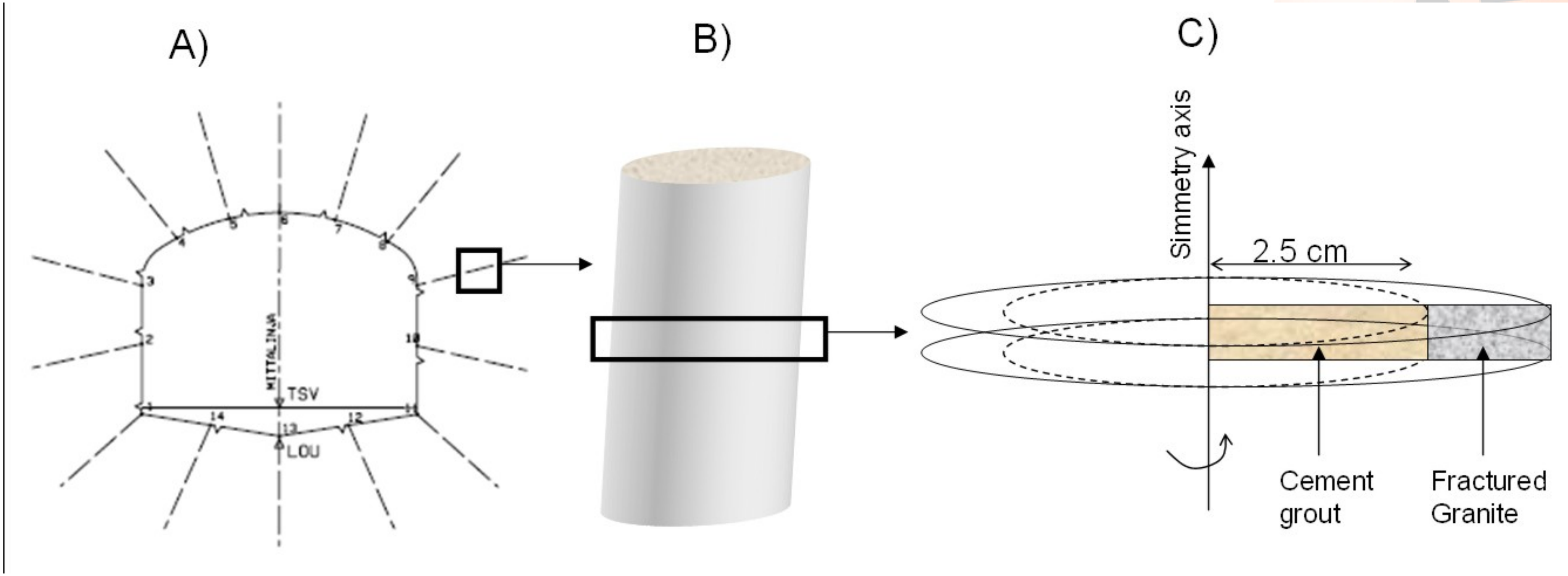
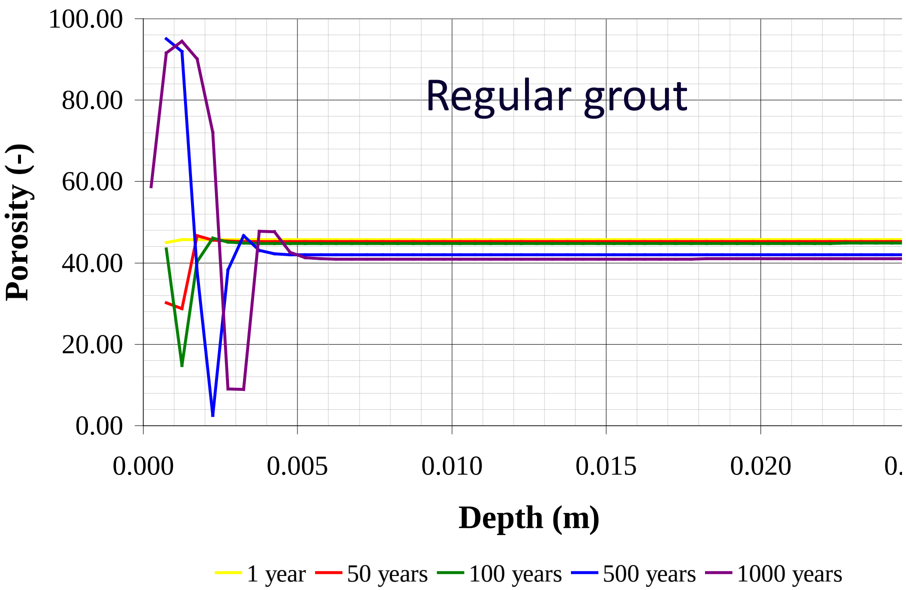
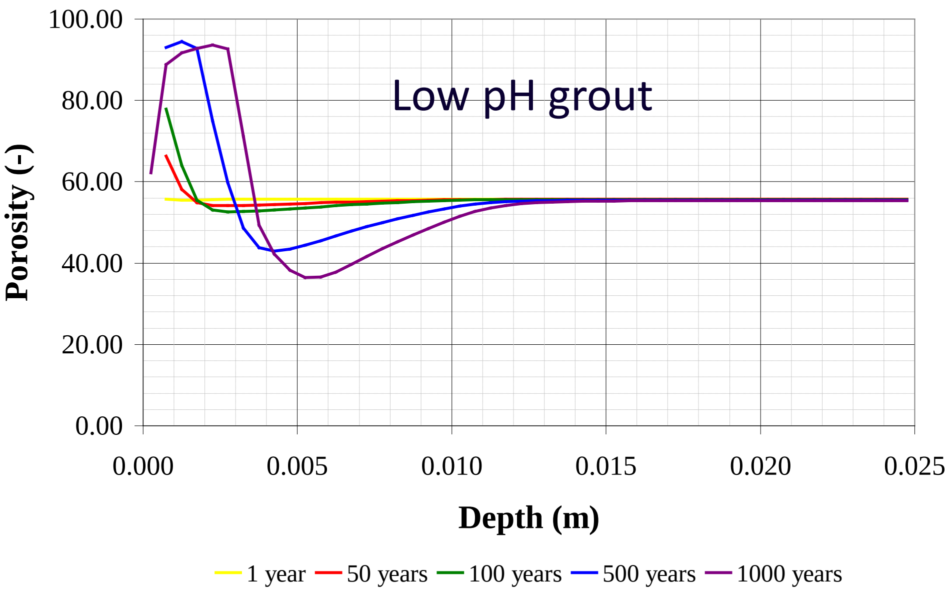
- CSH dissolution approaches-

Approach	Description	Flaws
LEA1. Thermodynamic equilibrium with pure solid phases.	Dissolution (sometimes using kinetic laws) of CSH-like crystalline phases (tobermorite, jennite, …) and precipitation of secondary phases.	NO incongruent dissolution.
LEA2. Thermodynamic equilibrium with solid solutions	**Dissolution of CSH phases with initial specified Ca/Si ratio. Arbitrary end members, not necessarily present in the system. Formation of new CSH with different Ca/Si ratio. Ability to reproduce incongruent dissolution using non-ideal SS.**	**Instantaneous re-equilibration of the SS with the fluid (Nernst-Berthelot approach).**
Kinetic dissolution-precipitation of CSH solid solutions . Carey and Lichtner	Implementation of the solid solution theory but using a discrete number of intermediate solids. Dissolution/precipitation is governed by (irreversible) kinetics (Doerner and Hoskins	Lack of kinetic data for many CSH phases.

> Simulation of the long-term degradation of grout







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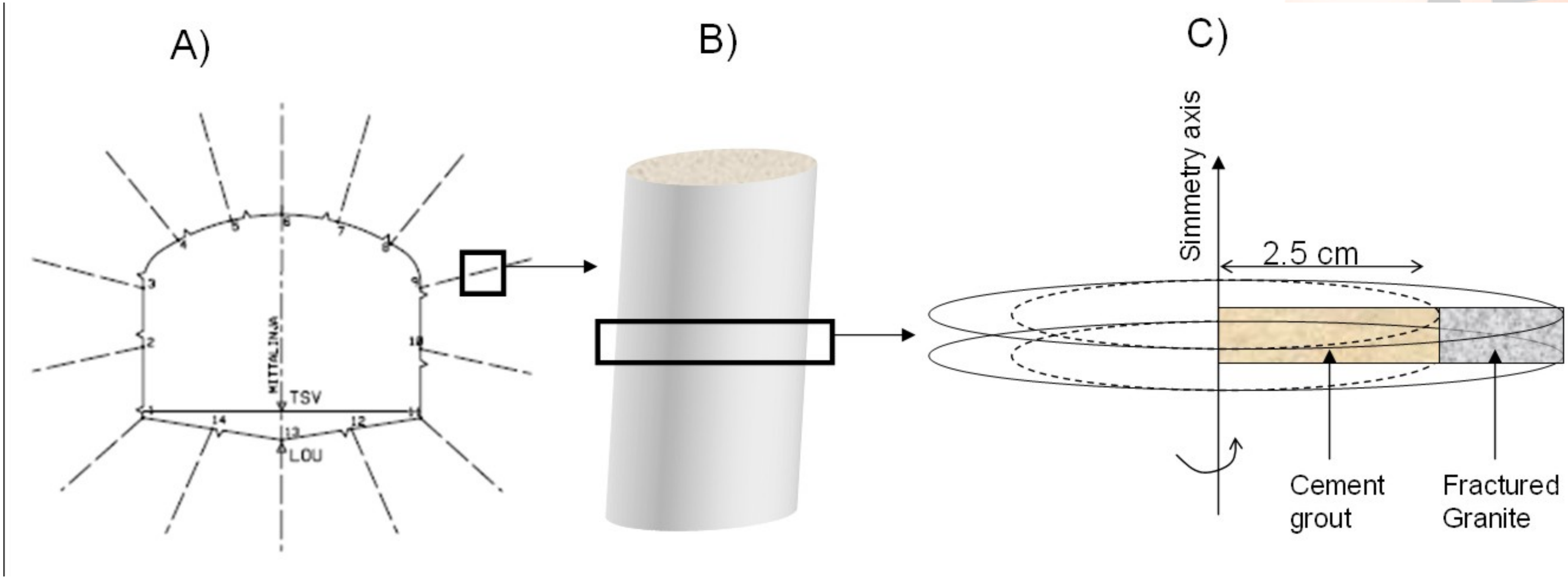
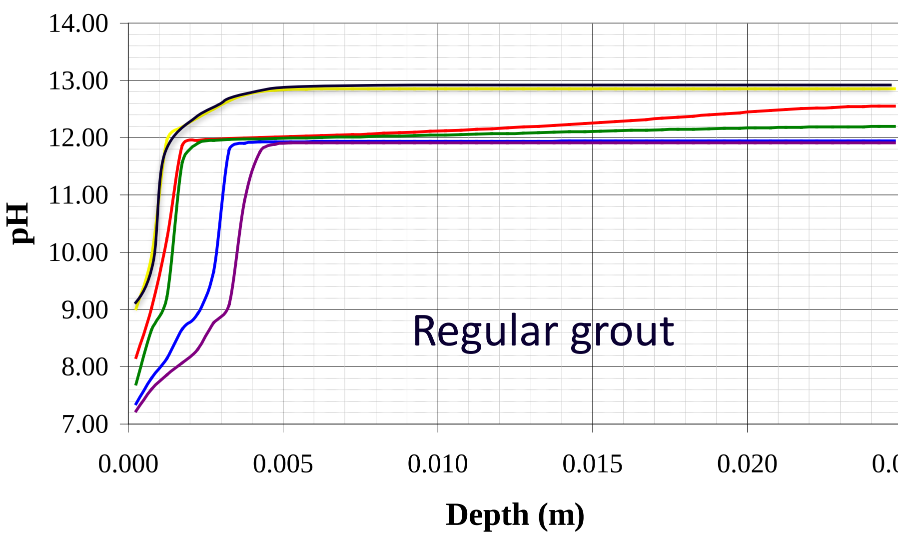
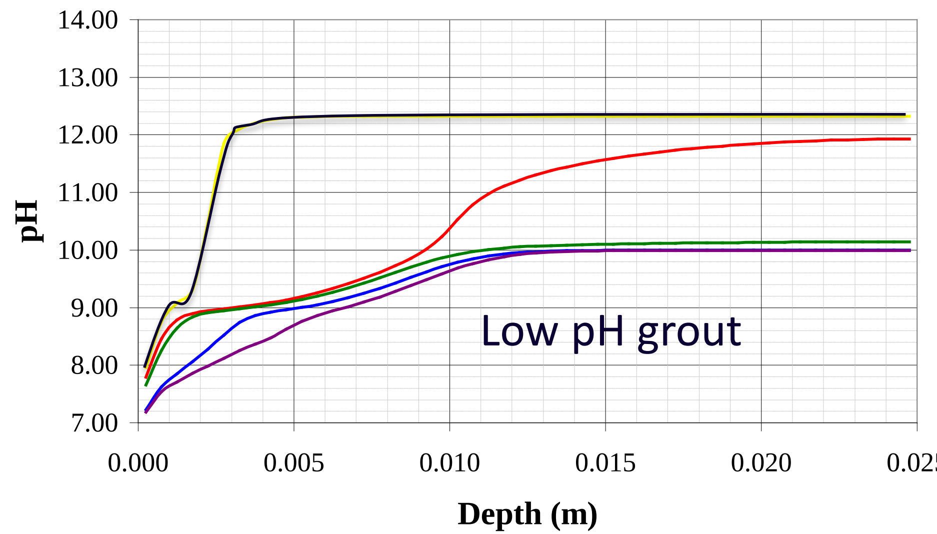




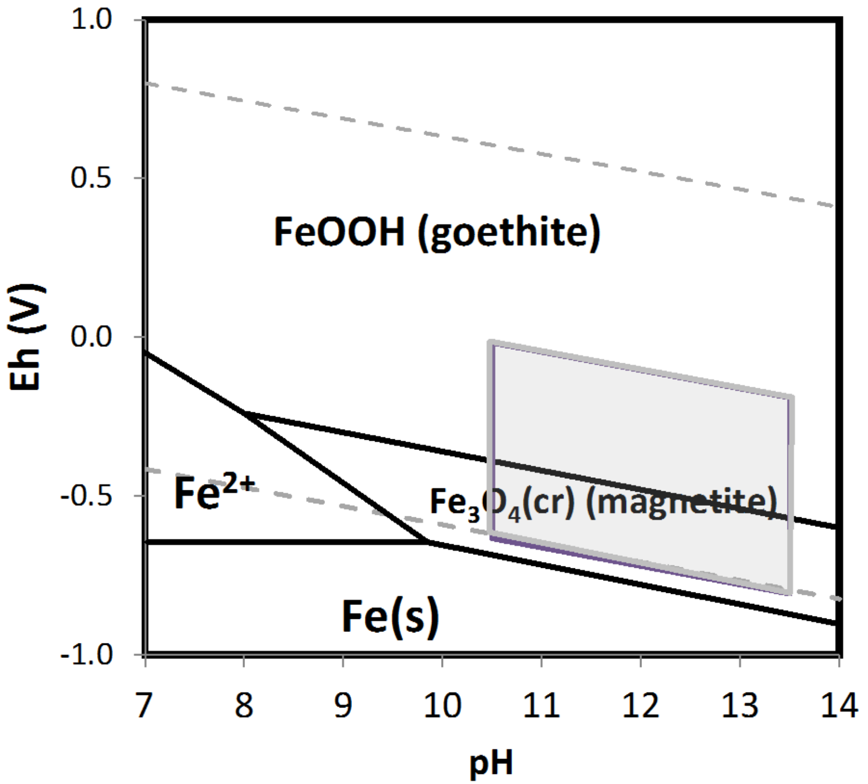


1 year — 50 years — 100 years — 500 years — 1000 years

Fundamental uncertainties

- Incongruent dissolution modeling: Pure phases vs. solid solutions
- Kinetics → Rates of precipitation/dissolution of intermediate phases
- Molar volume of intermediate phases (mainly CSH gels)
- Diffusion coefficients in cement porewater
- Validity of Fick's law vs. Nerst-Plank (electrochemical) diffusion
- HMC couplings (specially micro-cracking effects)

Eh/pH range. How does the presence of cement conditions Eh?



Scarcity of Eh measurements in cementitious systems

Critical for RN

pH	H_2O/H_2	Fe_3O_4/Fe_2O_3	Fe_3O_4/FeOOH	Fe_3O_4/HFO
13.5	-0.807	-0.721	-0.700	-0.190
12.5	-0.749	-0.663	-0.642	-0.132
10.5	-0.633	-0.547	-0.526	-0.016

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Solubility assessment: change in the controlling solid

Initial stage of concrete degradation

$CaU_2O_7 \cdot 3H_2O$

Final stage of concrete degradation

erelite(nat)

$CaU_2O_7 \cdot 3H_2O$

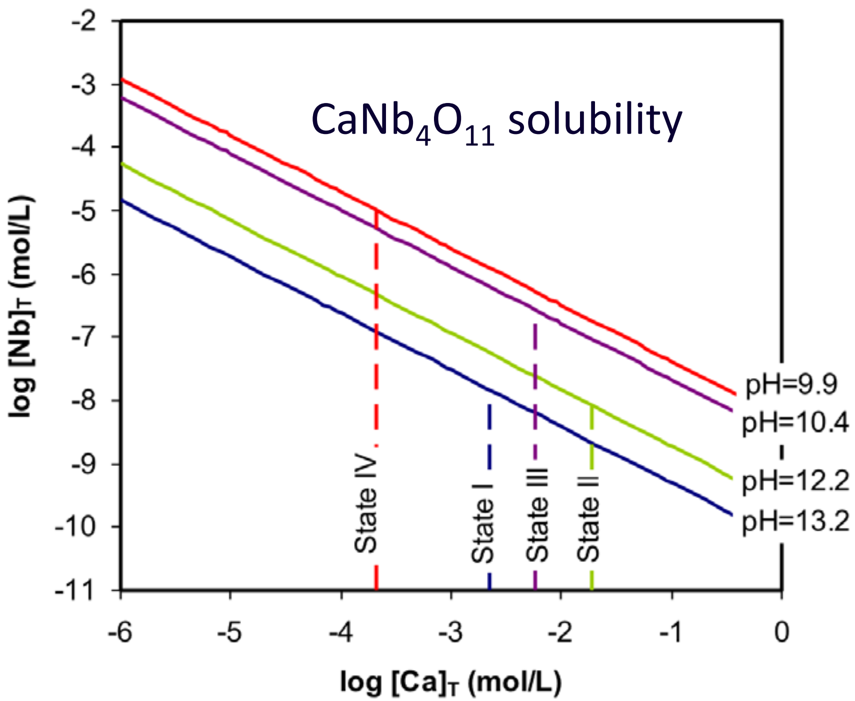
$UO_2 \cdot 2H_2O(am)$

	S-I	S-II	S-III	S-IV
pH	13.2	12.2	10.4	9.9
[Ca] (M)	$2.2 \cdot 10^{-3}$	$1.9 \cdot 10^{-2}$	$5.8 \cdot 10^{-3}$	$2.1 \cdot 10^{-4}$
[Si] (M)	$3 \cdot 10^{-6}$	$3 \cdot 10^{-5}$	$1.2 \cdot 10^{-3}$	a

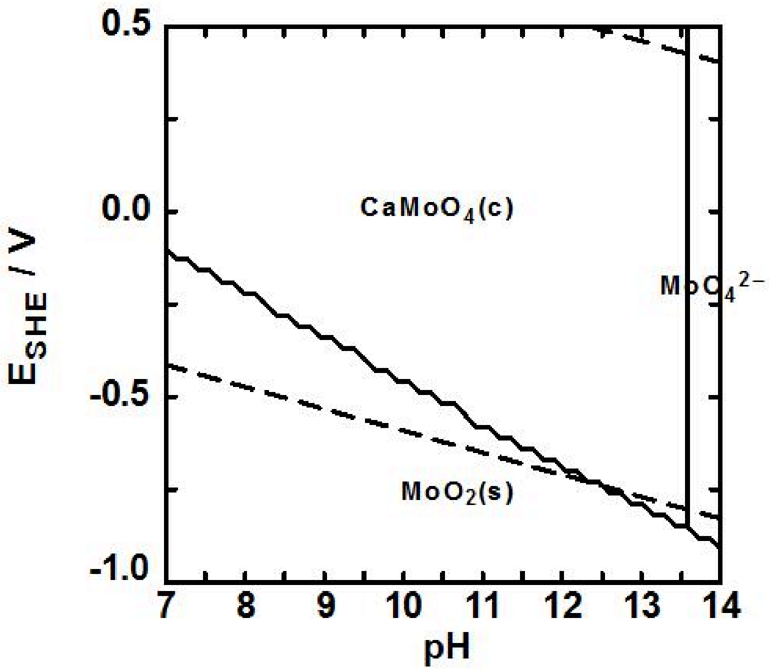
Solubility assessment

- Under conditioned cement systems:

special relevance for anion forming RN: Nb, Mo, Sn, Se, …



Thermodynamic data for Ca-RN phases



$$[Nb]\,predicted = 1.4613 \cdot e^{-1.3402 \cdot pH} \cdot \frac{[Ca]^{-0.8922}}{10^{2.6766}}$$

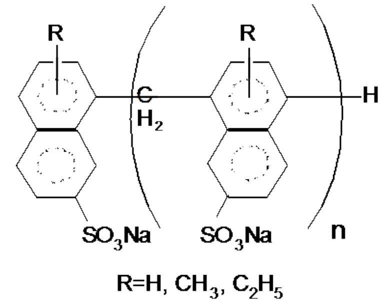
Talerico et al., 2004

Cement admixtures: speciation: solubility: sorption

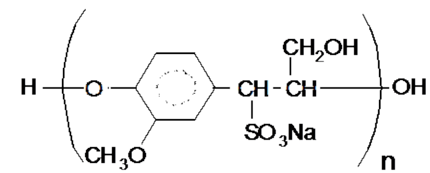
Type of admixture	Some substances (organics) used
Accelerators	Triethanolamina
Air detrainers	TBP
Air entraining	Alkylbenzene, sulphonates
Bonding	Rubber, PVC, PVA…
Corrosion inhibitors	Naϕ, PO4…
Damp proofing	CaNH4ϕ
Superplasticizers	Melamine Sulphon. Formaldehide…

- Sulphonated naphthalene-formaldehyde condensates (NS)
- Modified lignosulphonates (LS)
- Sulphonated melamine-formaldehyde condensates (MS)
- Polycarboxylate derivatives (PC)

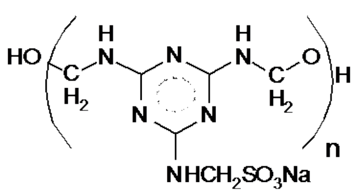
(1) NS



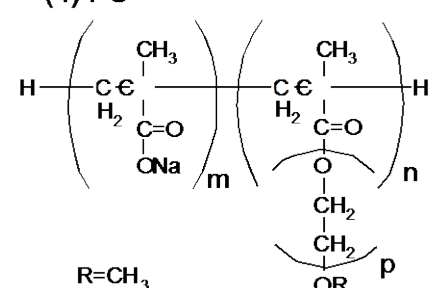
(2) LS



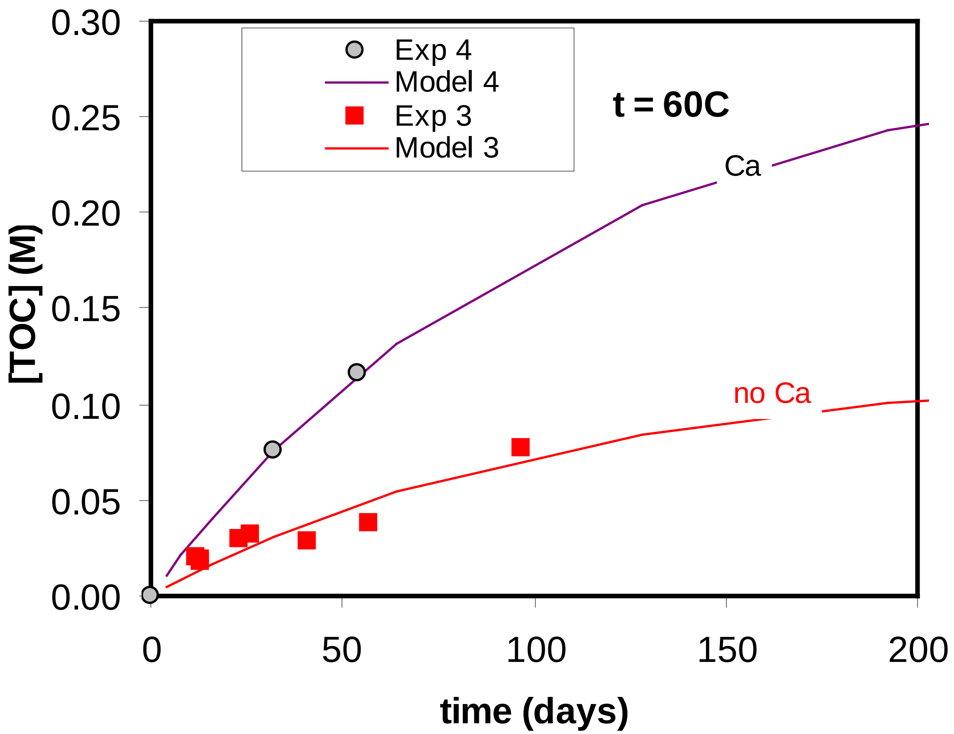
(3) MS



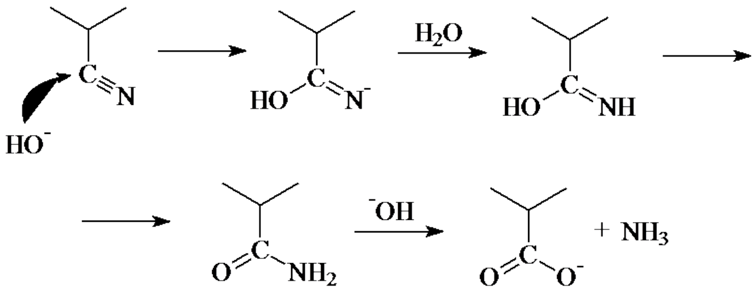
(4) PC



- Degradation of organic filter aid, PAN based: a maximum of a 20% of the degradation products identified



Empirical models: mechanistic quantification lacking



degradation of nitrile groups to carboxylates with ammonia release

(Duro et al., 2012)

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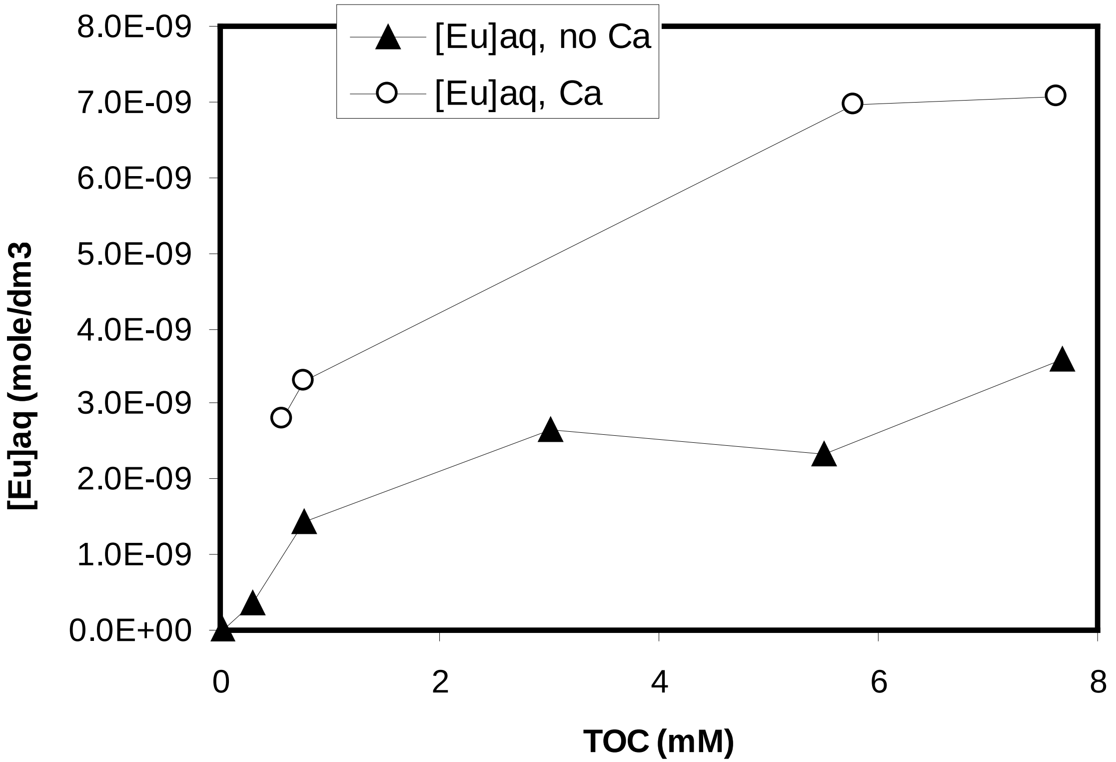
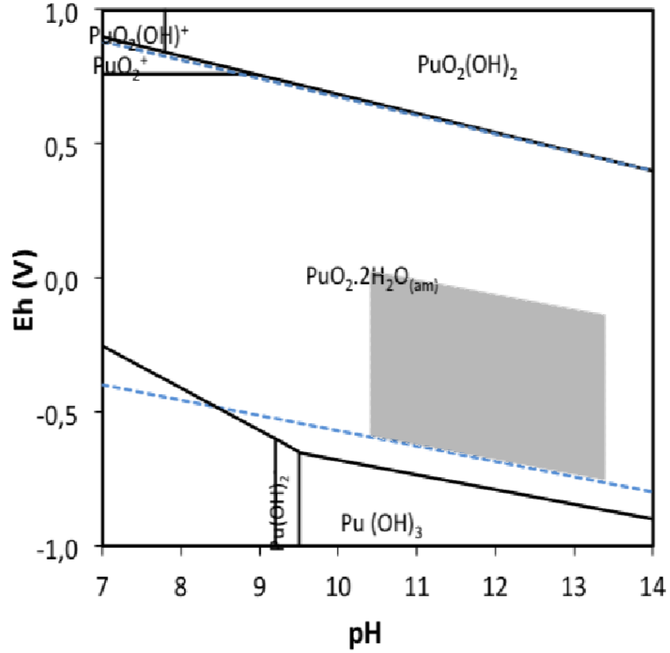
Example: Effect of degradation products of PAN on Eu sorption

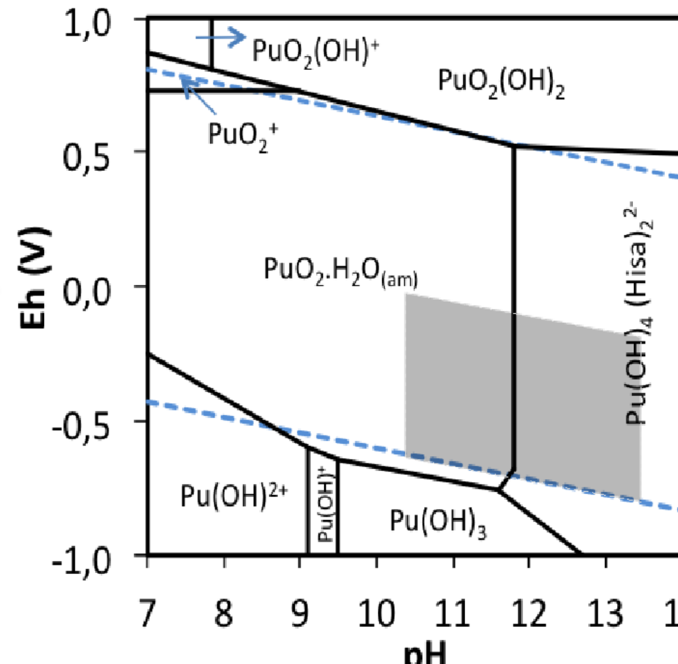


Quantification of retention changes: input data for SA is affected

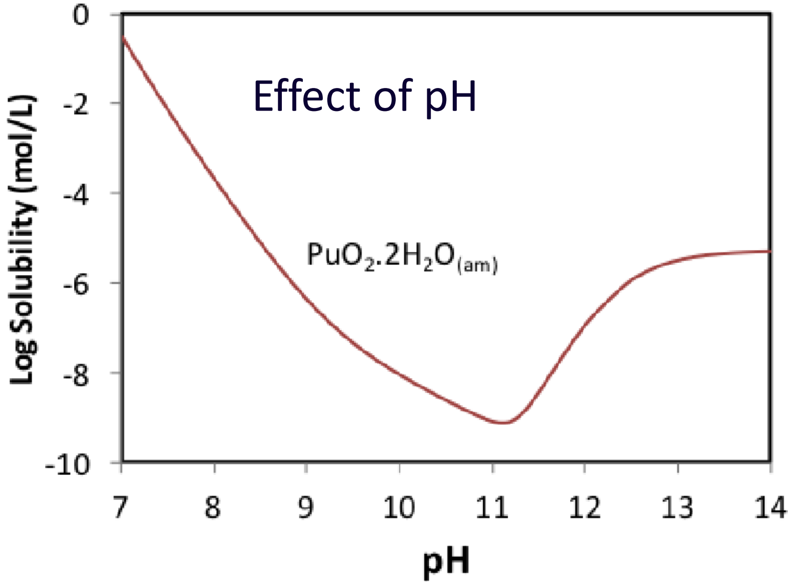
Organics in the wastes: speciation



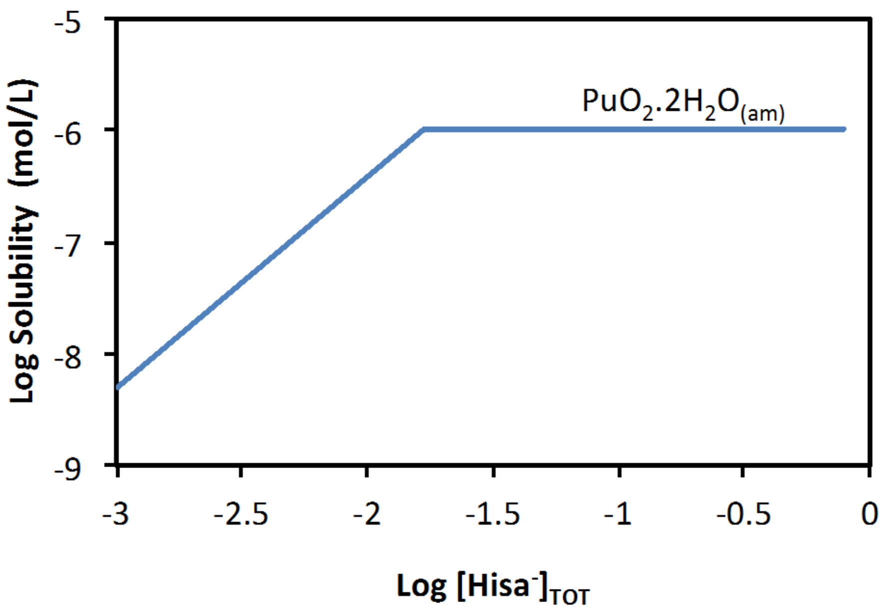
[ISA]
(1.6e-2M)



Effect on solubility



Effect of ISA



Modelling issues to consider for the new cement initiative

- Modelling of concrete degradation: coupling chemistry and physical properties (structural, hydrodynamics, ..)
- Effect of concrete degradation on near-field materials: swelling, porosity changes, retention properties
- Effect of high alkalinity on redox states: data and modellng
- High Ca concentrations: change in retention through sorption/solubility changes: mechanistic models to account for Ca effect
- Concrete is a source of complex complexing organics: how do they degrade? To which compounds? Which is the effect of these compounds on RN chemistry? On near-field materials? Bentonite, steels?
- How does the system (host-rock and repository) react? How long(in time and space) does it take to buffer the hyperalkaline plume, if at all?
- How low is low-pH cement?
- Can we take advantage of natural/human-made analogues?

Two concrete piers at the port of Progresso, Mexico. In the background one built with stainless steel reinforcement in 1941. In the foreground the remains of one built with carbon steel reinforcement in the 1960s.

Taken from Crossland (2006)