Interactions of actinides with cement corrosion products in chloride rich solutions: modelling and experimental results

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2nd International Workshop
“Mechanisms and modelling of waste / cement interactions”
October 12-16, 2008, Le Croisic

Acknowledgments

F. Geyer, S. Hilpp, M. Nesovic, M. Plaschke, J. Römer, E. Soballa and C. Walschburger (INE) for carrying out DTA, ICP-MS, OES, SEM-EDS, Raman and XRF analyses

R. Odoj and team for core drilling at FZJ-IEF6

K. Garbev (ITC-TAB) for assistance in evaluating XRD data

HMGU Asse and Bundesamt für Strahlenschutz, BfS, for technical support during probing of full-scale experiments and partial funding of the study

Background - Objectives

corrosion of cemented radioactive waste forms (LLW / ILW) under conditions of a repository in rock salt

durability of cemented waste forms in brine?

geochemical evolution of brine / secondary phases?

radionuclide retention?

- studying corrosion of cement forms in $MgCl_2$ brine
- studying interactions of Np, U with cement corrosion products

- comparison of modelling predictions to results of
    - short-term laboratory experiments with (Np, U doped) cement powders and
    - long-term full-scale experiments with (Np, U doped) doped waste simulates / ~200 dm^3 cement form blocks

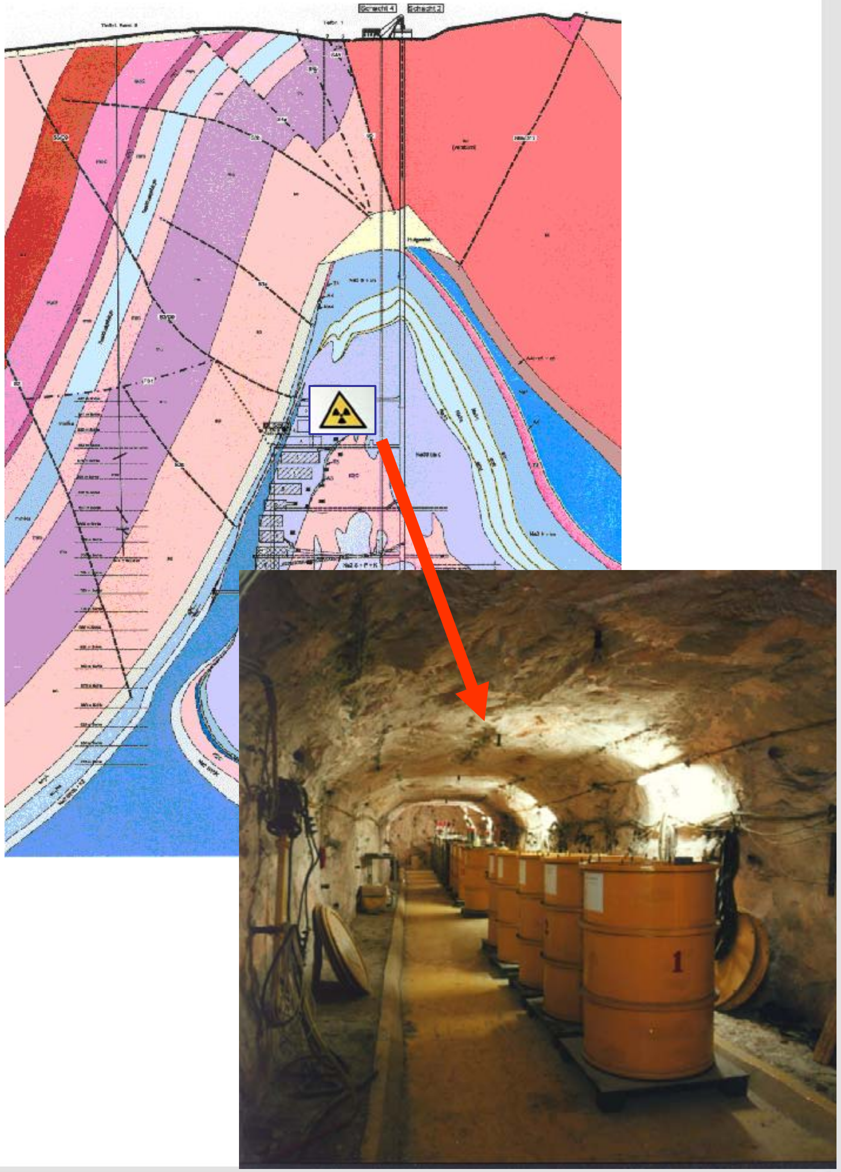
Long-term corrosion experiments

- static experiments since 1979/1989 (INE: 1996)

- simulated cemented waste samples doped with Cs_{nat} and *RN* (^{237}Np, U_{nat}, ^{137}Cs)
- waste simulates correspond to products of spent nuclear fuel reprocessing (*Purex* process; ~ 10 wt.% $NaNO_3$)

- Ordinary Portland Cement
- cement paste, water/cement ratio 0.3 – 0.5
- 160 dm^3 hardened cement blocks immersed in 400 dm^3 drums filled with leachant: $MgCl_2$-brine (“Q-brine”), NaCl brine, tap water

- experiments conducted at ambient conditions of LLW / ILW repository Asse salt mine (490-m level, 28° C)



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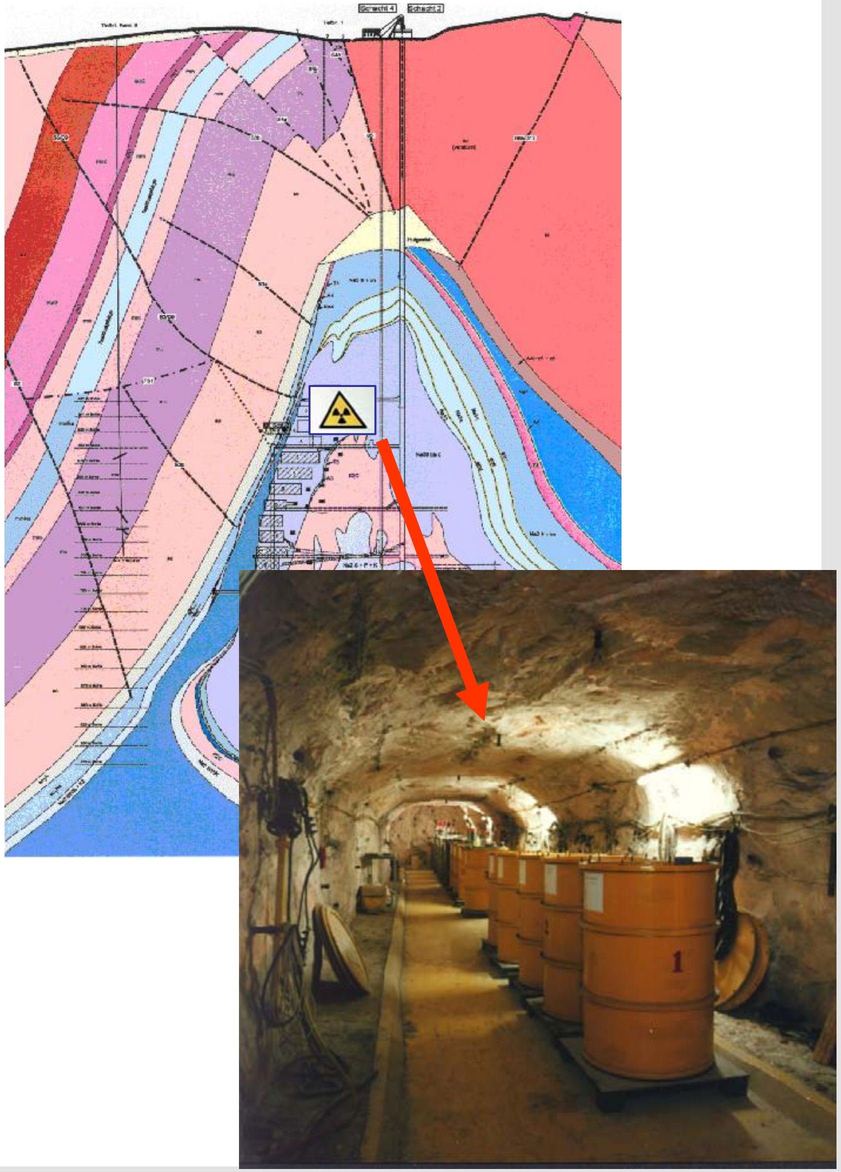


Initial composition of waste simulate (e.g. drum #33)

sample #33			
constituent	mass / kg	constituent	mass / kg
$Al(NO_3)_3 \cdot 9\ H_2O$	0.33	Portland cement	200
$Ca(NO_3)_2 \cdot 4\ H_2O$	0.92	water	99.02
$Cr(NO_3)_3 \cdot 9\ H_2O$	0.06	total	336.00
$Cu(NO_3)_2 \cdot 3\ H_2O$	0.06		
$Fe(NO_3)_3 \cdot 9\ H_2O$	0.29	water/cement	0.50
$Mg(NO_3)_2 \cdot 6\ H_2O$	0.82		
$Mn(NO_3)_2 \cdot 2\ H_2O$	0.03	waste content	11.0%
$Ni(NO_3)_2 \cdot 6\ H_2O$	0.04	RN content	
$Zn(NO_3)_2 \cdot 6\ H_2O$	0.07	U(nat)	5 MBq
Na-tartrat · 2 H_2O	0.61		
Na-citrat · 2 H_2O	0.59		
$Na_2HPO4 \cdot 12\ H_2O$	1.31		
$Na_2MoO_4 \cdot 2\ H_2O$	0.10		
NaNO3	31.11		
KNO_3	0.02		
Na-oxalate	0.52		
NaF	0.10		

- cement phases comprise ~90% of sample
- nitrates minor components
- accessories complexing agents (< 0.6 wt% in solid, inventory <3*10^{-2} molal in leachant: tartrate, citrate, oxalate
- radionuclides doped in trace concentrations (few grams Np per sample 1 kg U_{nat} per sample)

significant complexation of U(VI), Np(V) at aqueous concentrations of “free” chelating agents > 10^{-2} molal
=> scavenging of chelats by Ca^{2+}, Mg^{2+} …?

Core drilling in glove box

after approaching steady state (with respect to solution composition) termination & core drilling

- dry drilling performed at Research Centre Jülich
- due to production of contaminated dust drilling in glove box

- samples from various depth and lateral positions

Laboratory experiments: Materials and methods

(A) cement / brine equilibration experiments

inactive corrosion of OPC paste (w/c = 0.4) in Q-, R- and conctr. $MgCl_2$-brine at various $mass_{cement}$ / $volume_{brine}$ ratios ($0.001 < m/V < 1.1$ g cm^{-3})

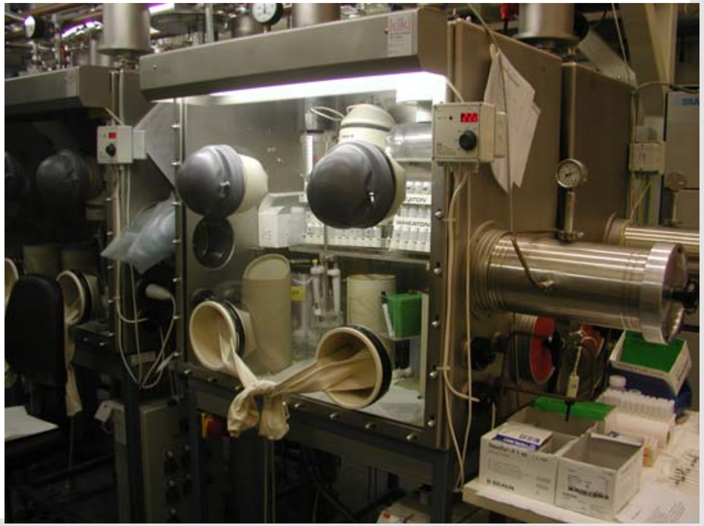
(B) Np, U sorption experiments

adding aliquots of $^{237}Np(V)$, $^{233}U(VI)$ stock solutions to equilibrated cement / brine systems (variation in m_{cement} / V_{brine})

(C) Np, U solubility experiments

- dissolving Np, U solids in equilibrated solution of (A) cement / brine equilibration
- dissolving Np, U solids in pure $MgCl_2$- and NaCl-solutions (pH variation; NpO_2, NpO_2OH, UO_3:$2H_2O$, $Na_2UO_2O(OH)$)

static experiments running for 6 – 24 months;
Ar atmosphere (pO_2, $pCO_2 \leq 1$ ppm);
powders of hardened cement paste (A) and cement corrosion product (B), respectively

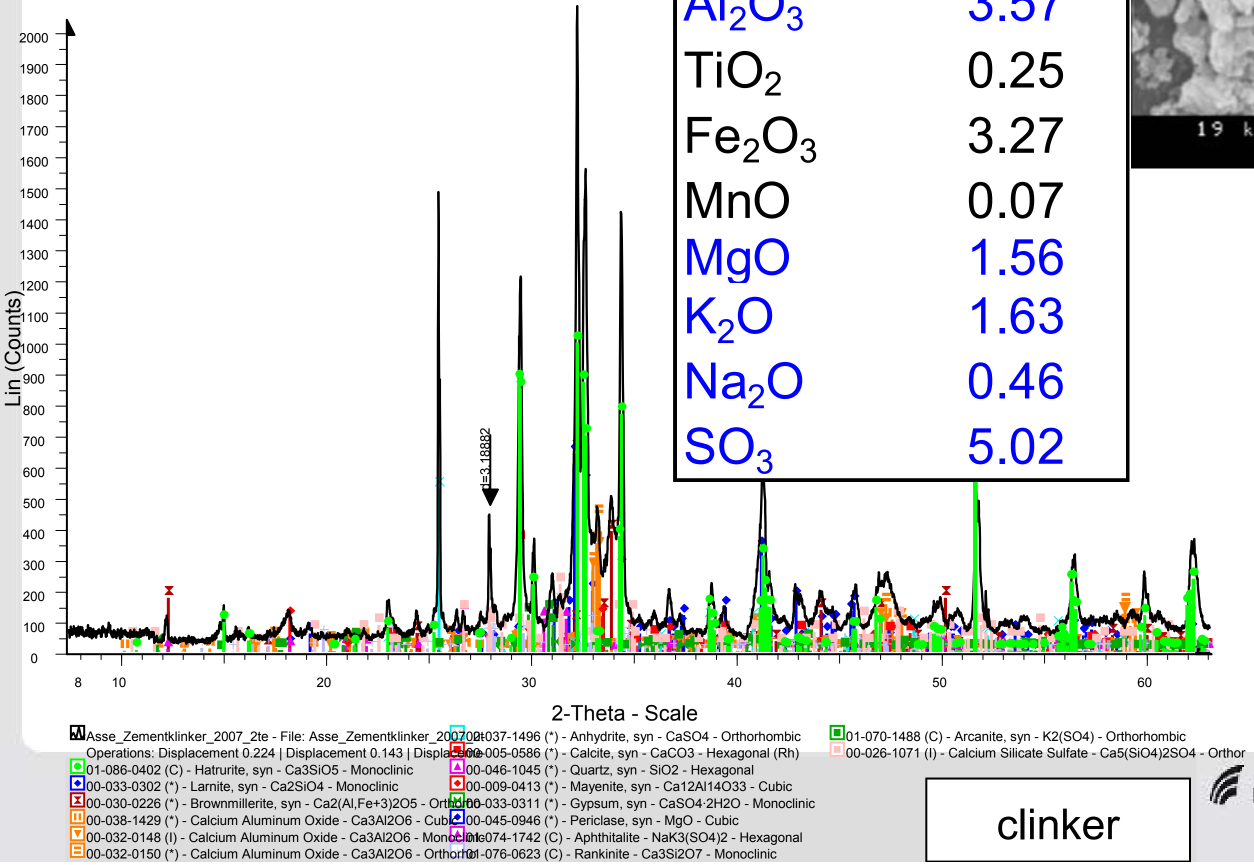


Laboratory experiments: solid material

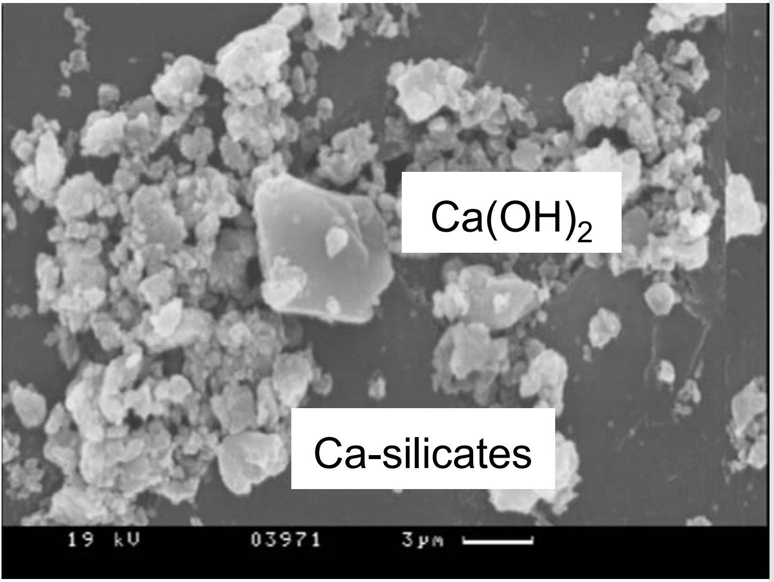
(A) cement / brine equilibration experiments

OPC paste, w/c = 0.4, <u>without</u> additives (NO_3^- …)

oxide	content wt%
CaO	66.87
SiO_2	17.29
Al_2O_3	3.57
TiO_2	0.25
Fe_2O_3	3.27
MnO	0.07
MgO	1.56
K_2O	1.63
Na_2O	0.46
SO_3	5.02



clinker

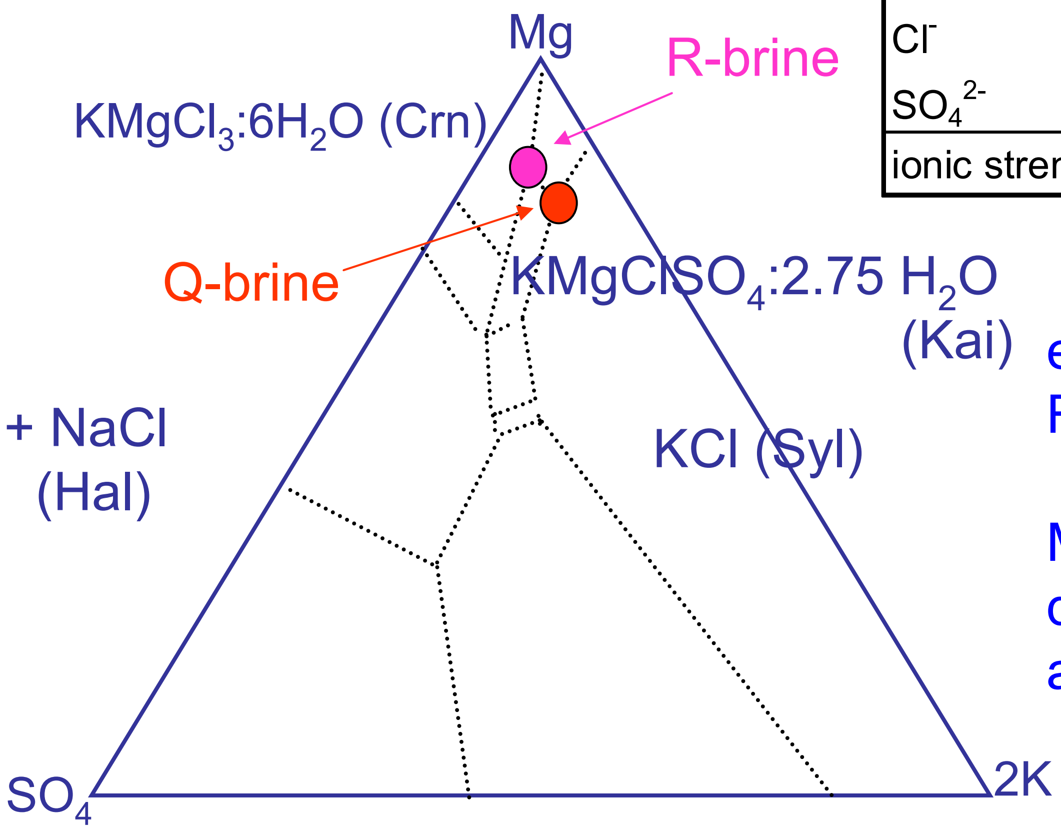


clinker phases:
silicocarnotite,
belite / larnite,
brownmillerite,
gypsum,
quartz,
calcite,
periclase (…)

$MgCl_2$ rich leachants: initial compositions

equilibrated brine in system
$NaCl-KCl-MgCl_2-Na_2SO_4-H_2O$

		R-brine	Q-brine
Mg^{2+}	mol $(kg\ H_2O)^{-1}$	5.2	4.2
Na^+	mol $(kg\ H_2O)^{-1}$	0.2	0.4
K^+	mol $(kg\ H_2O)^{-1}$	0.3	0.5
Cl^-	mol $(kg\ H_2O)^{-1}$	10	9
SO_4^{2-}	mol $(kg\ H_2O)^{-1}$	0.4	0.2
ionic strength	val $(kg\ H_2O)^{-1}$	16.5	13.8



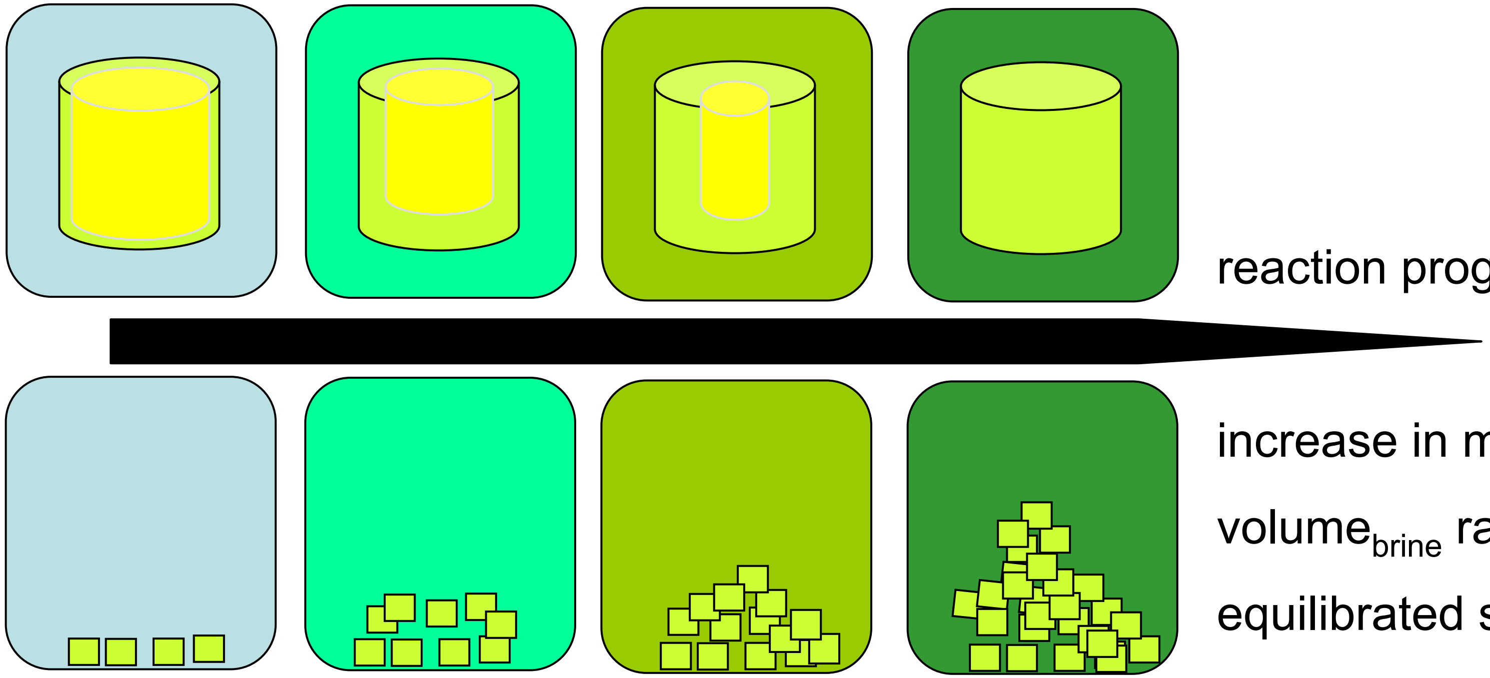
experiments with Q-brine, R-brine, 4 molal $MgCl_2$ solution

$MgCl_2$ brines slightly acidic due to Mg^{2+} hydrolysis and aggressive vs. OPC

Geochemical simulations: conceptual model

Reaction path modeling:

- initial thermodynamic equilibrium between solution and solid phase computed
- infinitesimal amount of reactant cement paste "added" to solution
- new equilibrium calculated including precipitation of super-saturated solid phases
- in next step, again infinitesimal amount of reactant added to altered solution (…)



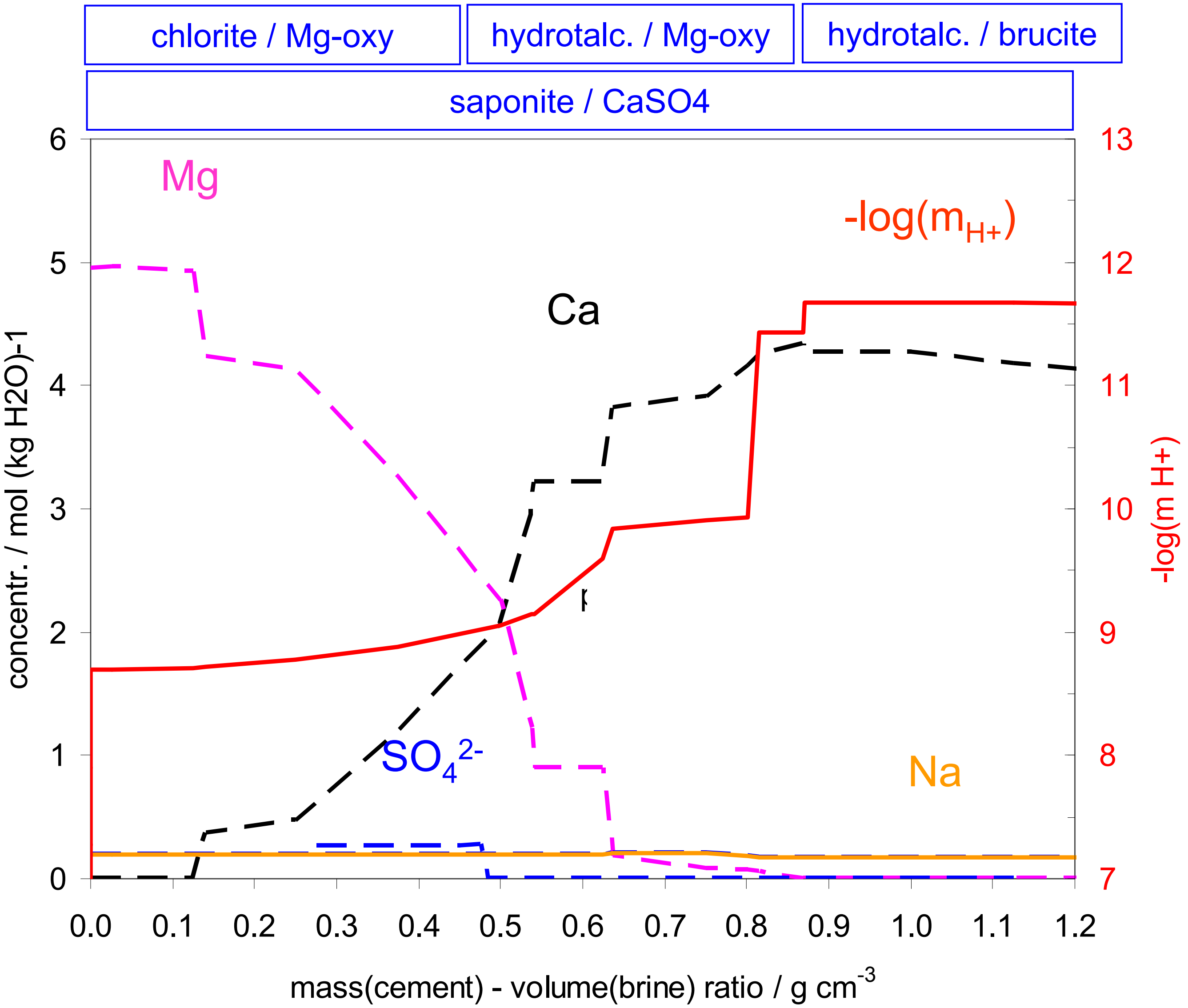
reaction progress (time)

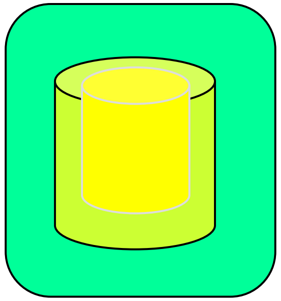
increase in $\text{mass}_{\text{cement}}$ to $\text{volume}_{\text{brine}}$ ratio of equilibrated systems

Calculation methods

- EQ3/6 software package (Geochemist's Workbench)
- concentrated salt solutions: Pitzer activity model
- Harvie-Moller-Weare database Na-K-Mg-Ca-H-Cl-SO4-OH-HCO3-CO3-CO2-H2O including brucite, Mg-oxychloride, Ca-oxychlorides, calcite, Mg-hydroxocarbonates …
- simplifications necessary due to lack of thermodynamic data (e.g. Pitzer parameters)
- EQ3/6 data0.hmw database extended for solubility products, log K_{sp}, complexation constants, log β, and ion-interaction coefficients (Pitzer parameters):
  - Np(V), U(VI) solids, aqueous species, Pitzer param. for Mg-Na-H-Cl-OH-H_2O
  - Al, Si aqueous species, Pitzer parameters
  - solubility products, log K_{sp}, of alumosilicate / aluminate endmembers:
    hydrotalcite 4MgO.Al2O3.10H2O, quartz SiO2,
    chlorite endmembers, e.g. clinochlore Mg5Al2Si3O10(OH)8,
    smectite endmembers e.g. Ca-saponite Ca.165Mg3Al.33Si3.67O10(OH)2

Modeling predictions

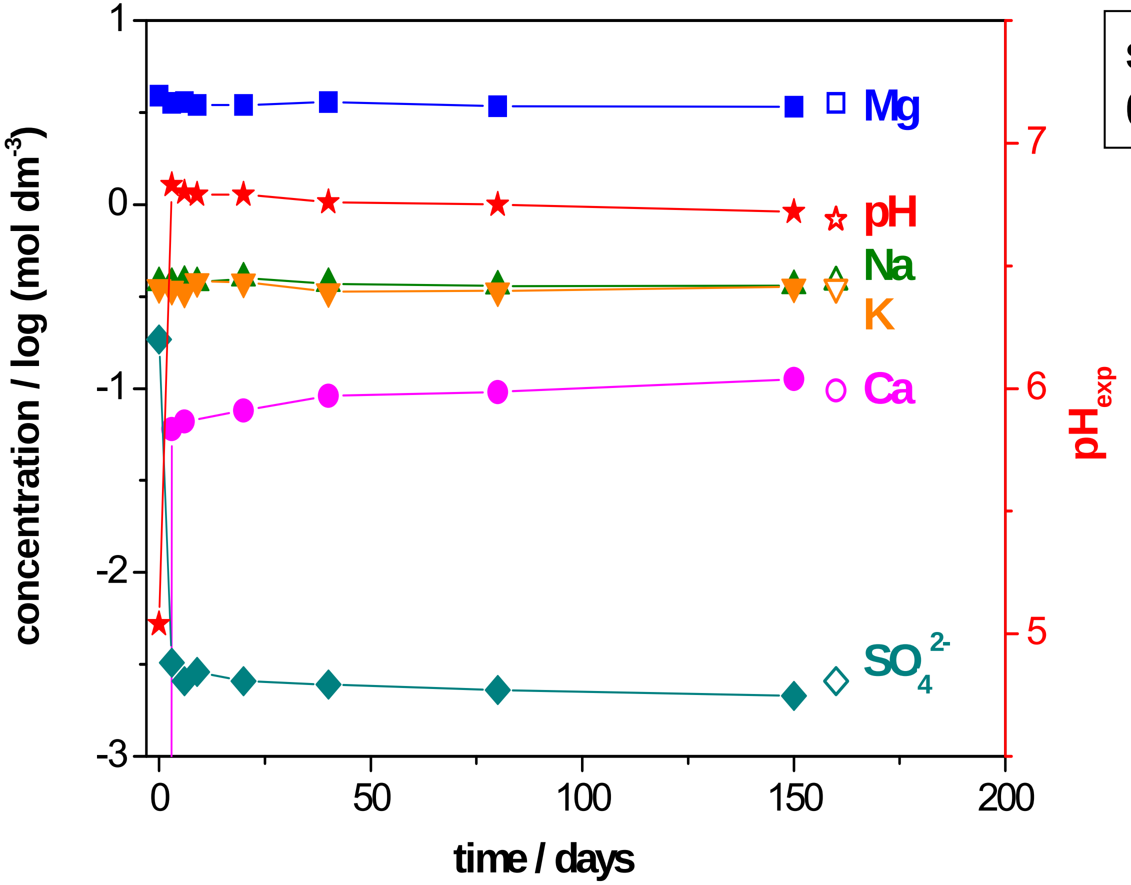




- Mg ⇔ Ca exchange in solid phases
- Mg(aq) decrease
- Ca(aq) increase
- pH increase
- Na constant
- SO_4^{2-}, Al, Si relatively low conctr.

Results of laboratory experiments

corrosion of OPC powder in $MgCl_2$ brine



e.g. $mass_{cement}$ / $volume_{brine}$ 0.1 g cm^{-3}

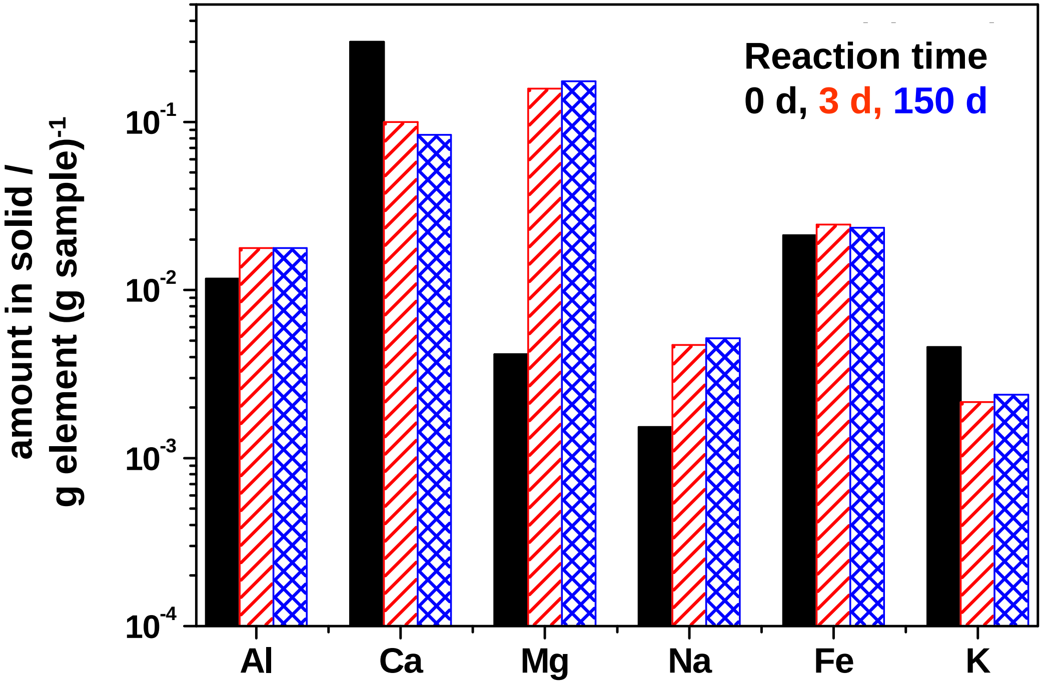
specific experimental series for
$0.001 < m/V < 1.1$ g cm^{-3}

Solution composition
within few weeks approaching
apparent steady-state
$\Delta C/\Delta t \to 0$ when
$\Delta C \leq$ analytical uncertainty

In concentrated $MgCl_2$ solution
high detection limit
Si, Al conctr. < detection limit

Results of laboratory experiments

corrosion of OPC powder in $MgCl_2$ brine



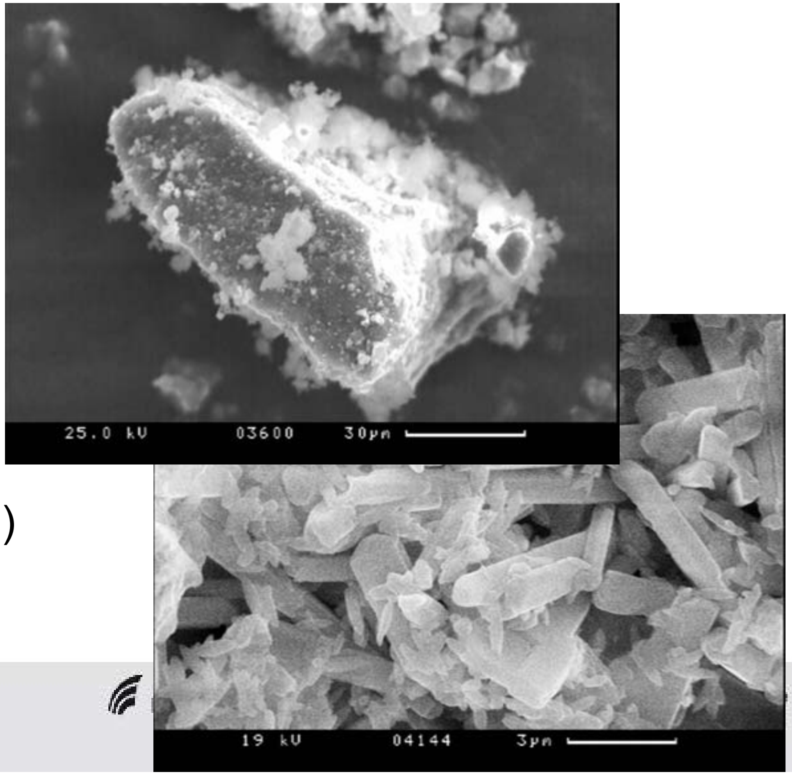
e.g. $mass_{cement}$ / $volume_{brine}$ 0.1 g cm^{-3}

XRF: Composition of solid material

- depletion of Ca content
- strong increase in Mg
- no significant change in Fe (Si)

minor components

- increase in Na, decrease in K, no significant change in Al

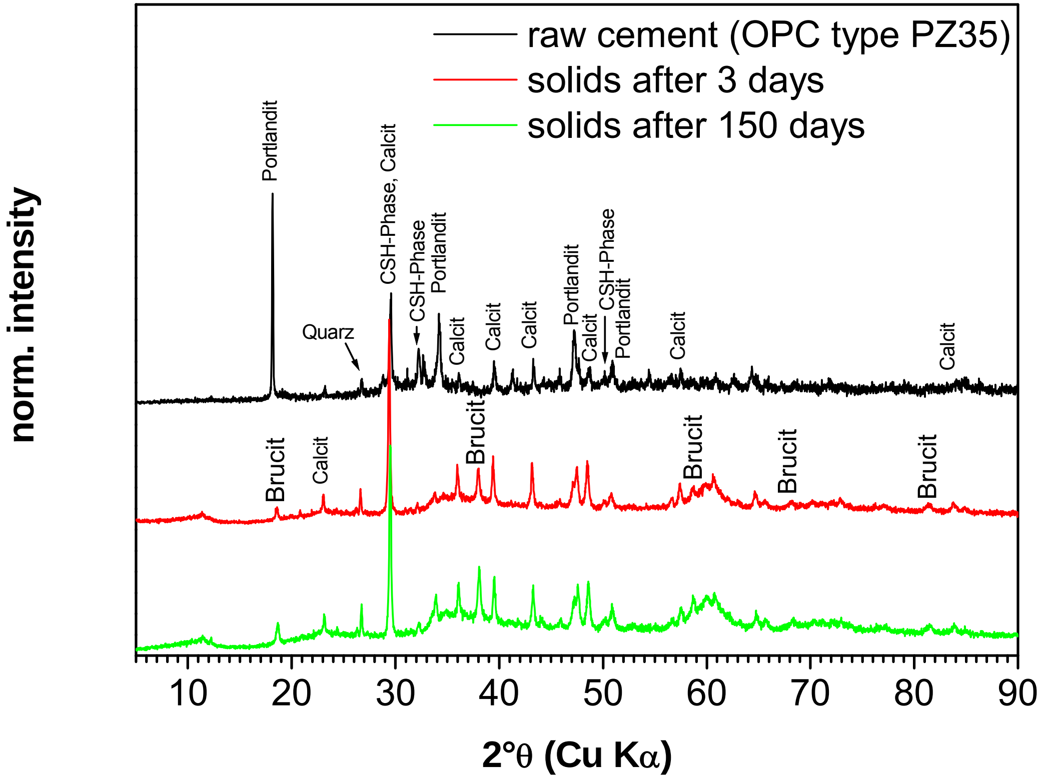


SEM-EDS: secondary phases

- Mg-oxychloride (except m/V > 0.75 g cm^{-3})
- Mg-silicates and Mg-Ca-silicates
- halite

Results of laboratory experiments

corrosion of OPC powder in $MgCl_2$ brine



e.g. $\text{mass}_{\text{cement}}$ / $\text{volume}_{\text{brine}}$ 0.1 g cm^{-3}

Summary of XRD results

- steady state after few weeks – no significant difference in mineralogical composition to samples after 150 days
- secondary phases: Mg-oxychloride (except m/V > 0.75), hydrotalcite, gypsum, (brucite, quartz)
- hydration relics: hydrogarnet
- clinker relics: silicocarnotite, belite / larnite, brownmillerite

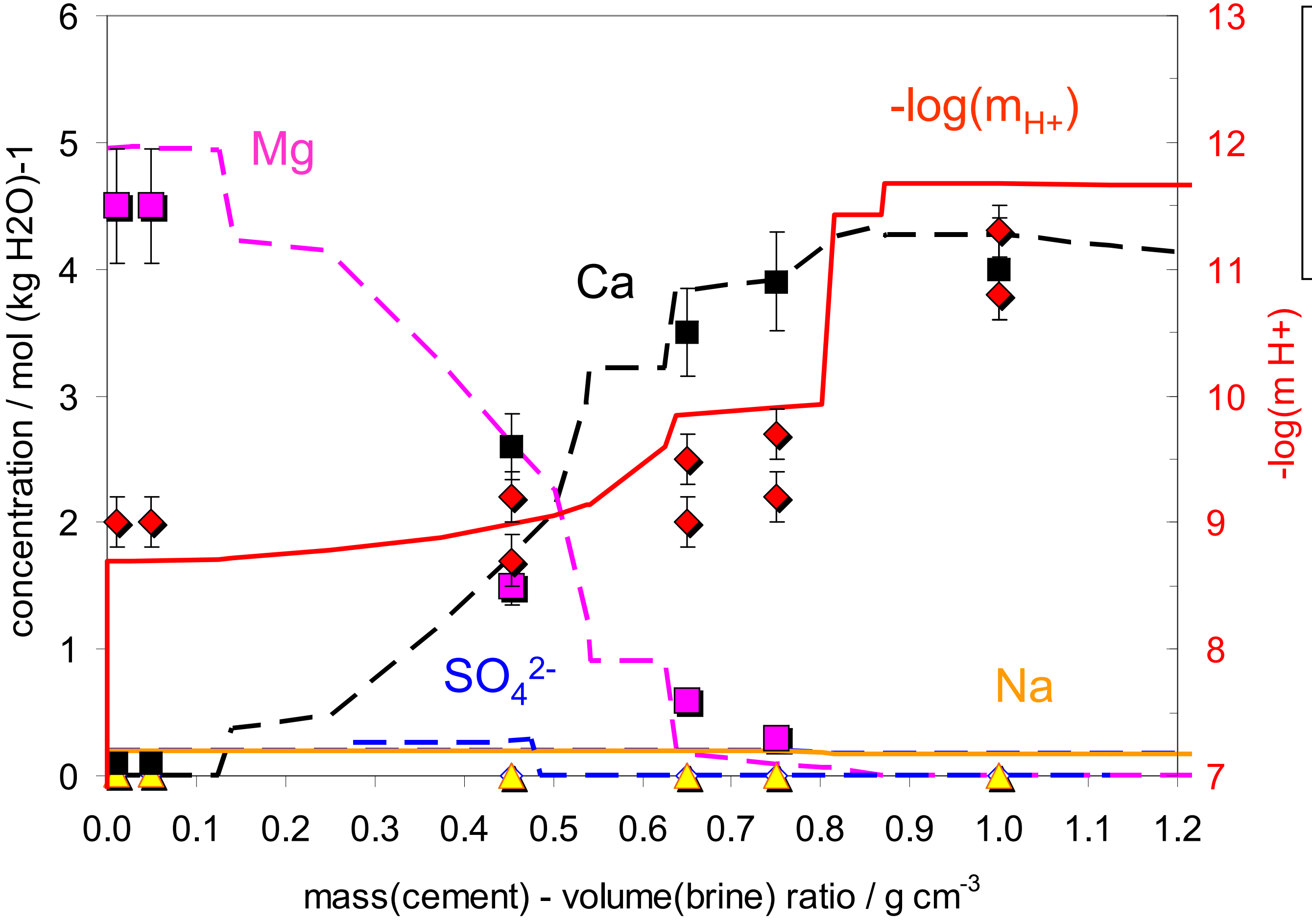
Comparison simulations with lab results

chlorite / Mg-oxy

hydrotalc. / Mg-oxy

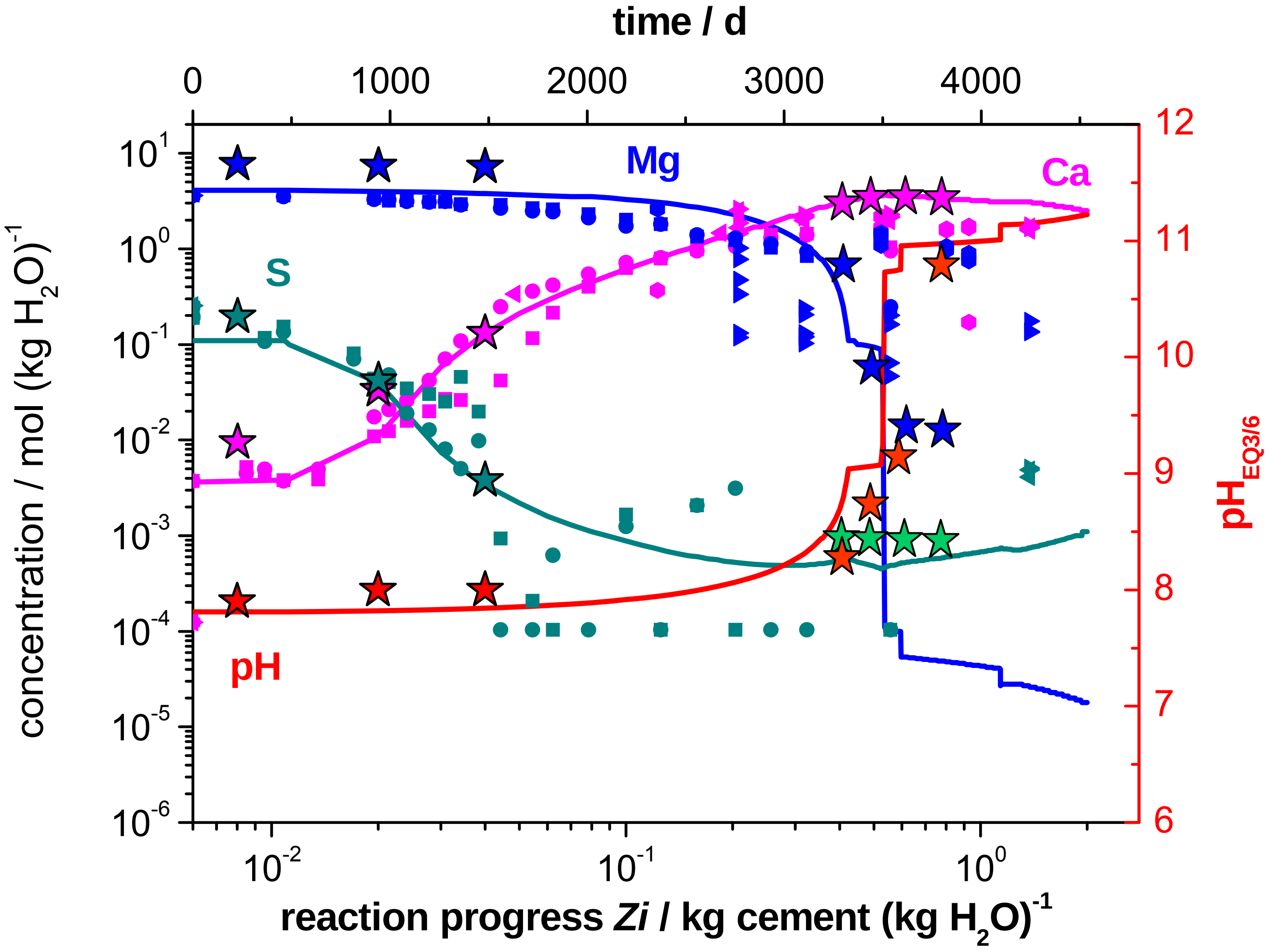
hydrotalc. / brucite

saponite / CaSO4



Experimental data:
Steady state results of
specific experim. series
OPC in R-brine
0.001 < m/V <1.1 g cm^{-3}

Comparison results of simulation with results of laboratory / full-scale experiments

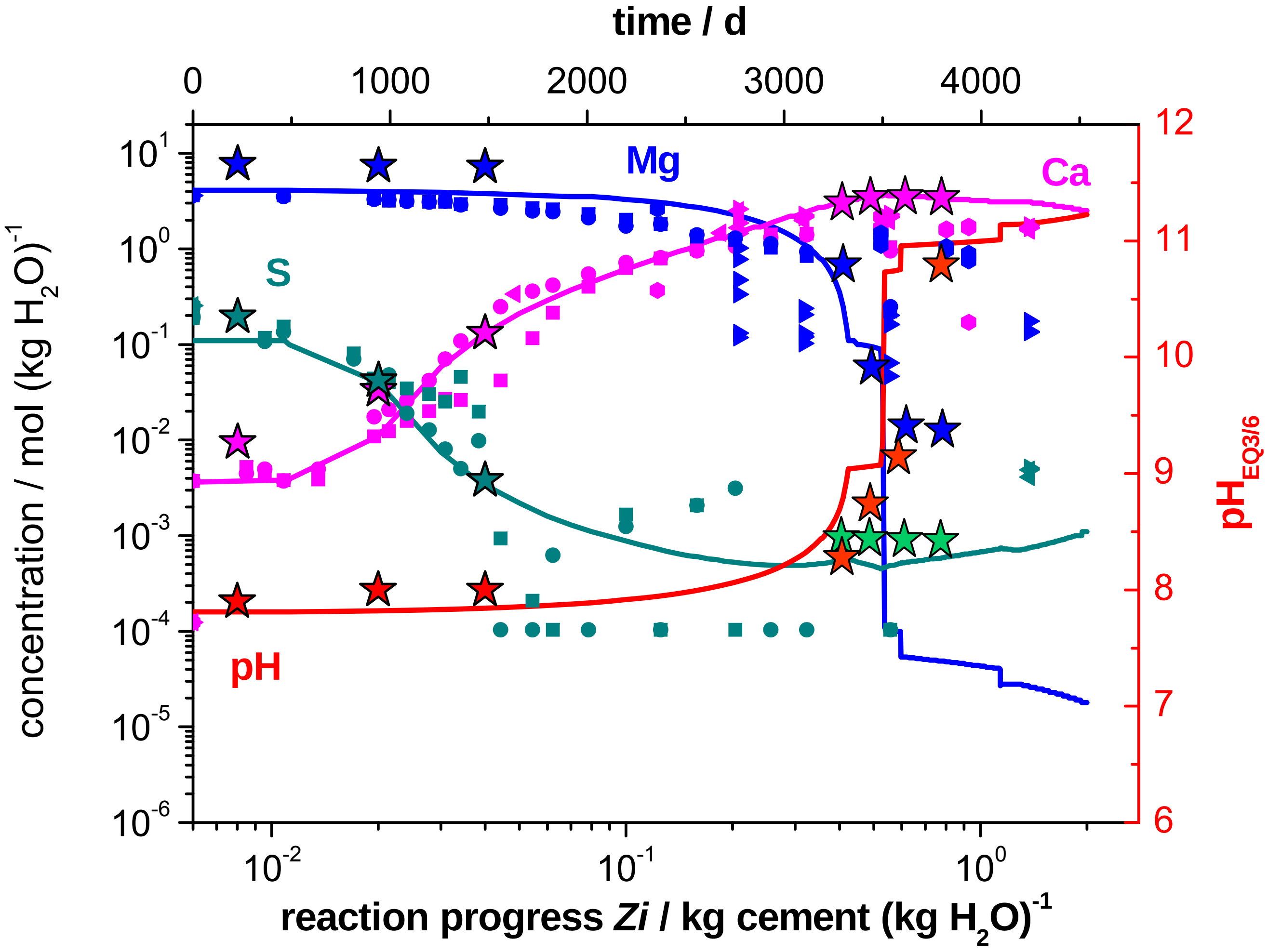


<u>Laboratory experiments:</u>
Steady state results
OPC in R-brine / Q-brine
(*stars*)

<u>Full-scale experiments:</u>
temporal evolution of
waste simulate in Q-brine
(*small symbols*)

<u>Simulation:</u>
evolution of OPC in
Q-brine (*lines*)

Comparison results of simulation with results of laboratory / full-scale experiments



With respect to
solution composition

waste components don't affect significantly overall solution evolution

up-scaling of lab results (volume scale; powder / cement block)

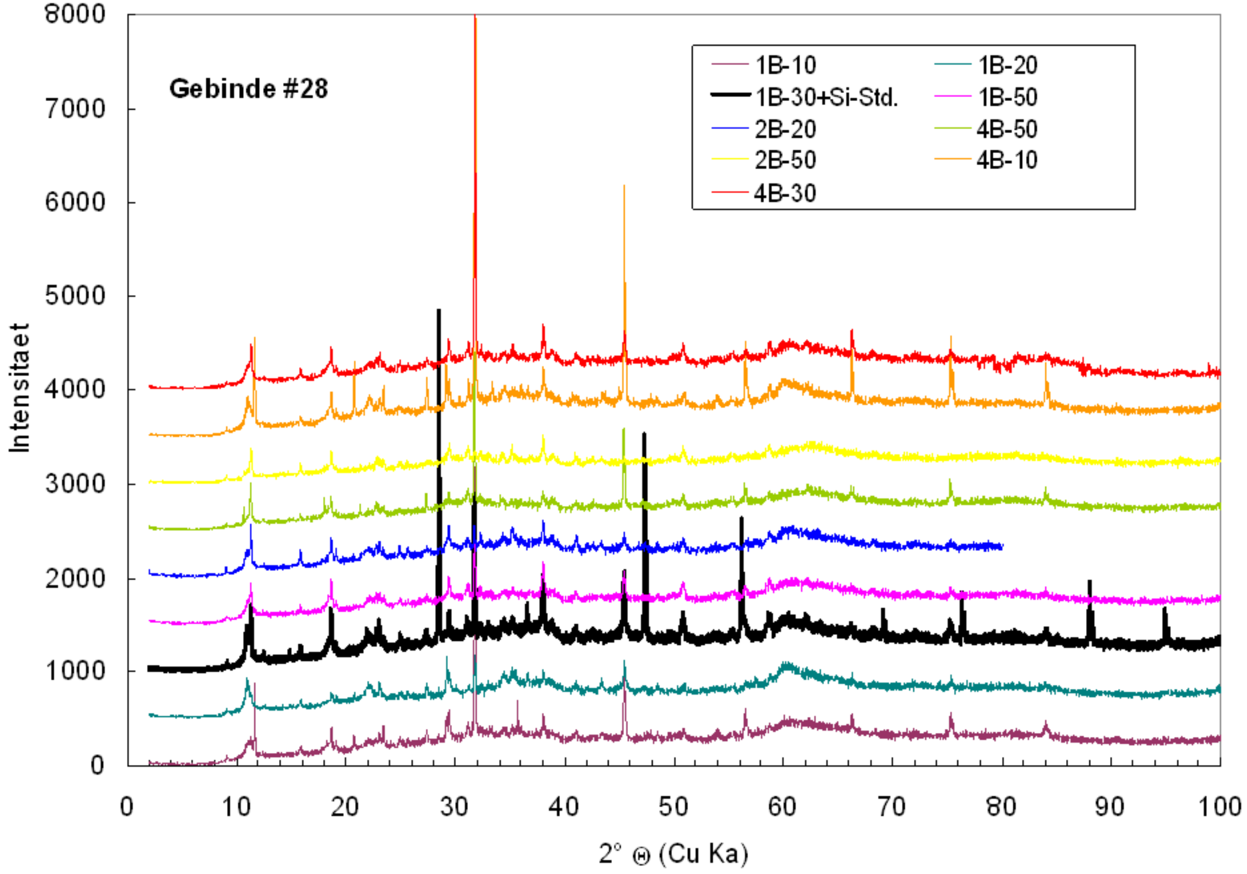
Fair agreement between results of simulation with results of laboratory / full-scale experiments

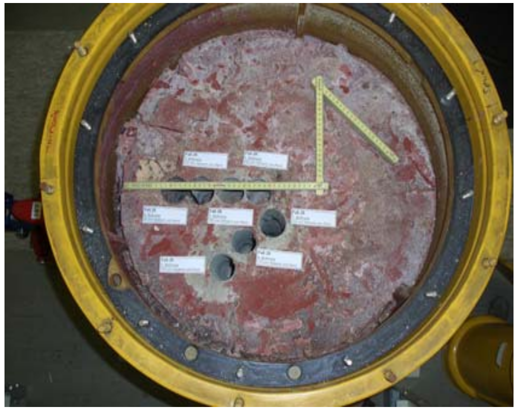
Full-scale experiment(s) close to equilibrium?

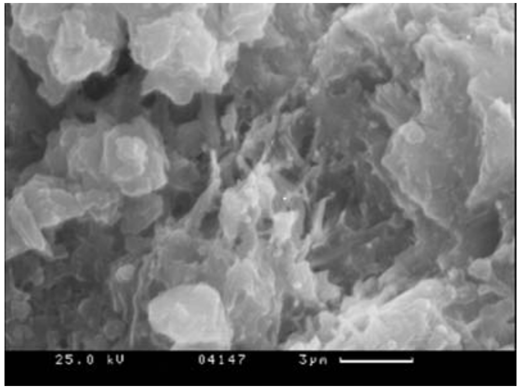
Full-scale experiments: XRD and SEM-EDS

characterization of final solid samples

Homogenous lateral and vertical distribution of mineral phases (except calcite enrichment in first 10 cm)



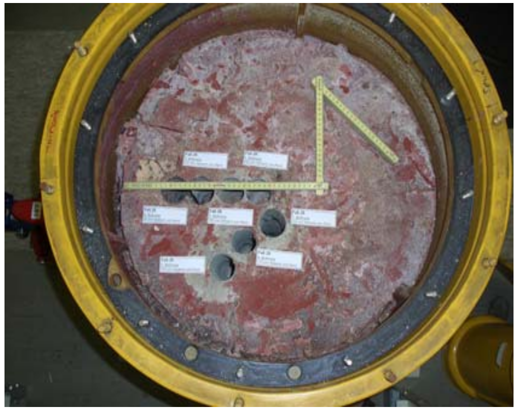




Hydrotalcite, ettringite,
gypsum, halite,
brucite +/- Mg-oxychloride
calcite (mainly surface zone)

Full-scale experiments: nitrate and DTA-TG

analyses of final solid samples



Summary of nitrate analyses

no significant radical / vertical variation in nitrate content
(additionally steady state in aqueous nitrate concentration)

Summary of DTA-TG analyses

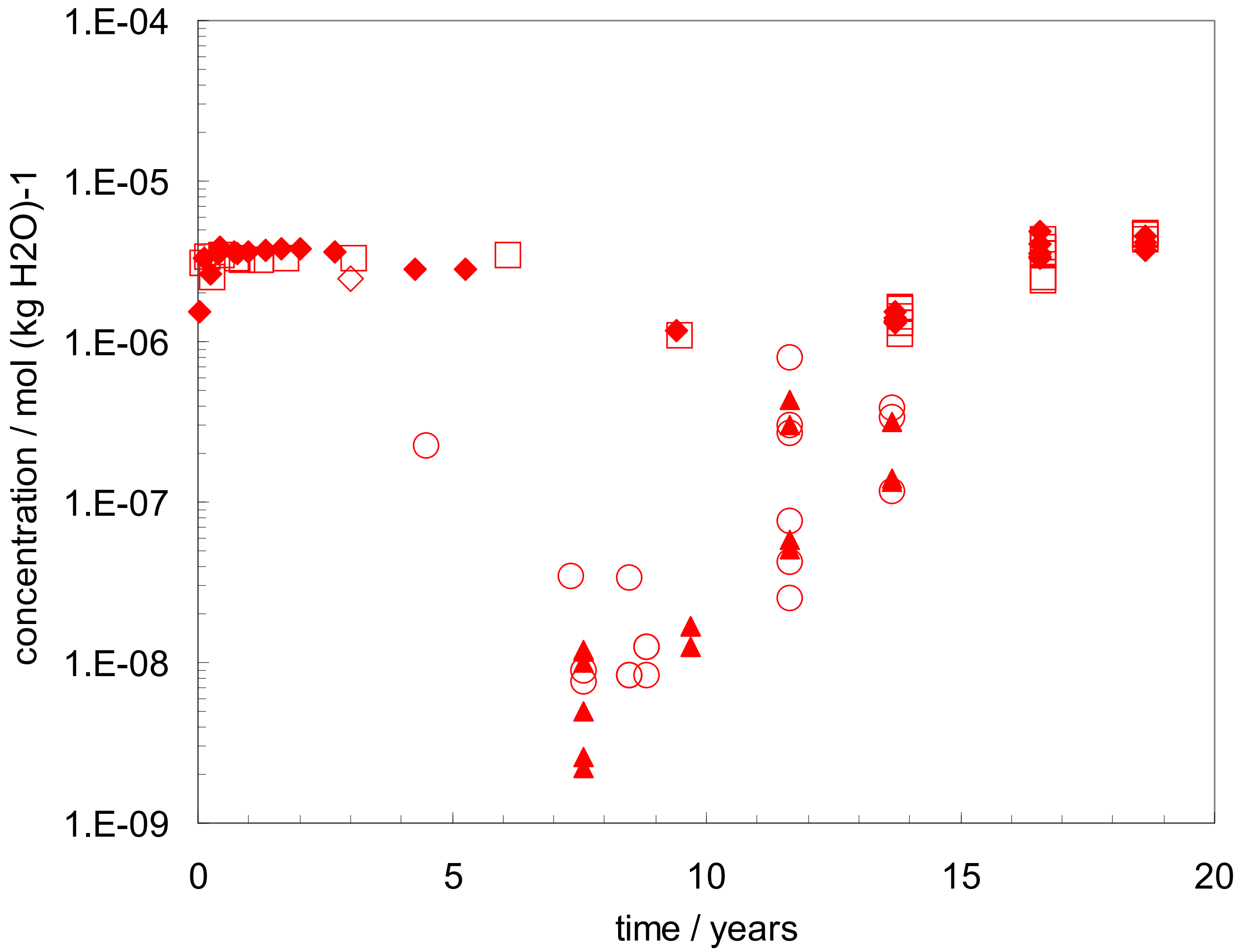
- homogenous distribution of phases containing
  OH-, SO_3-, CO_2-groups (homogenous DTA-TG patterns)
- exception calcite enrichment in outer surface zone
  calcite content in internal zones < 2 wt%

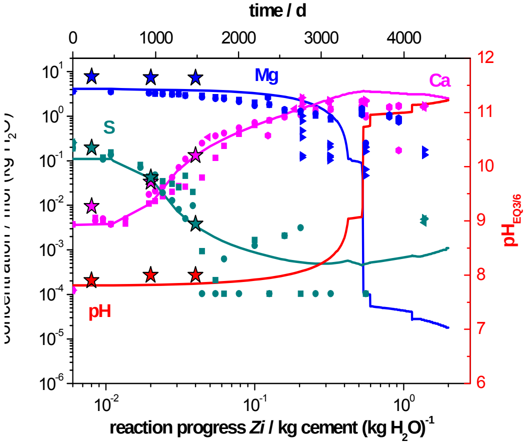
- homogenous distribution of mineral phases in corroded cement blocks
- formation of stable secondary phases with respect to solution composition
  (hydrotalcite, gypsum, halite, brucite +/- Mg-oxychloride)

indicate **equilibration of cement / brine systems** of full-scale experiments within ~25 years

Variation of U concentration with time:

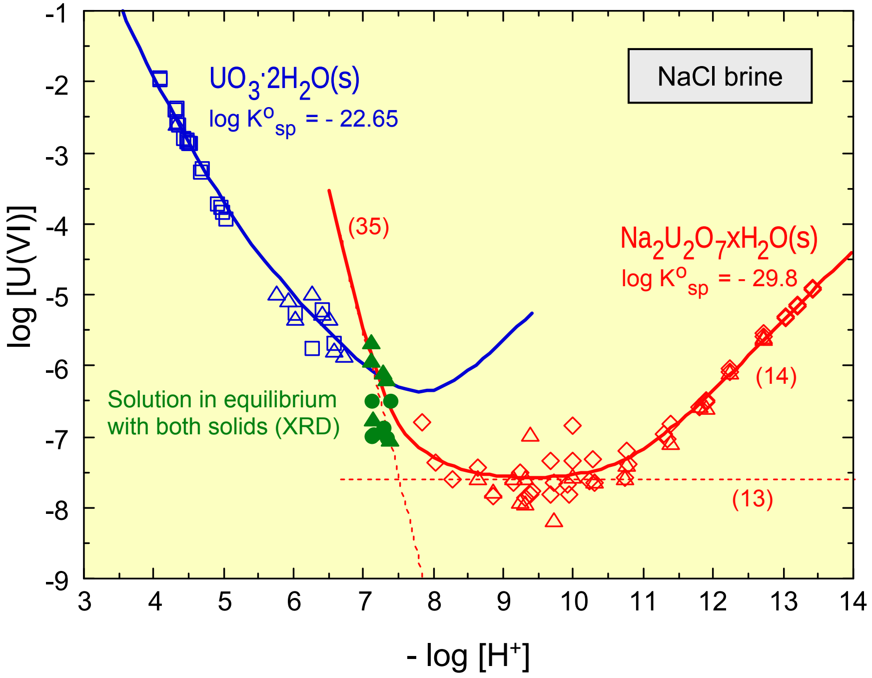
full-scale experiments

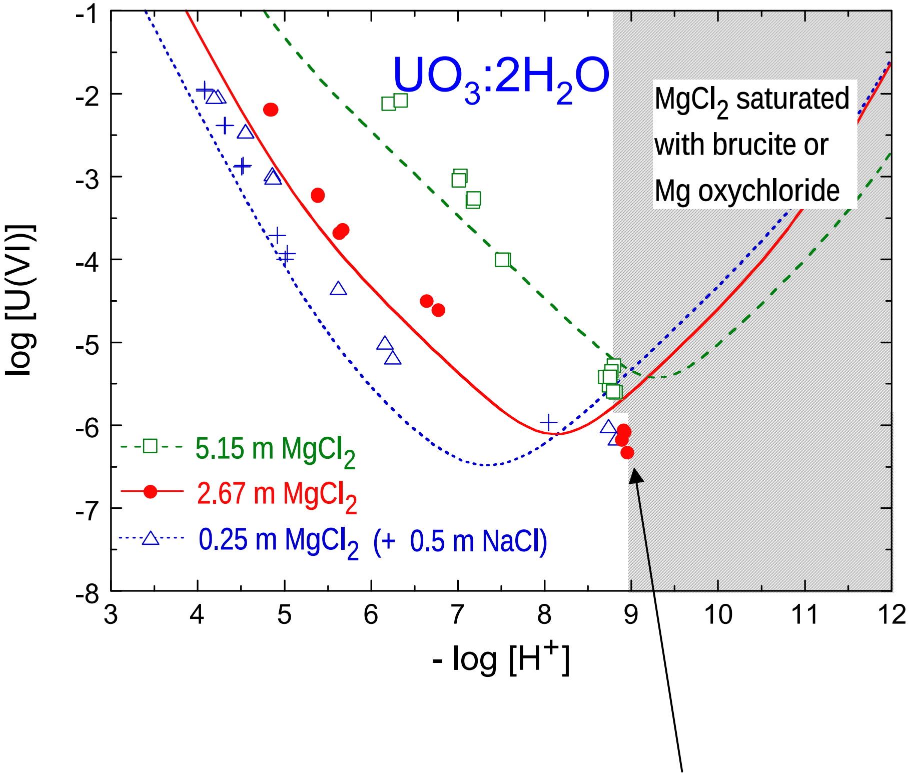




changes in solution composition affects changes in U conctr.

Laboratory experiments on U(VI) solubility

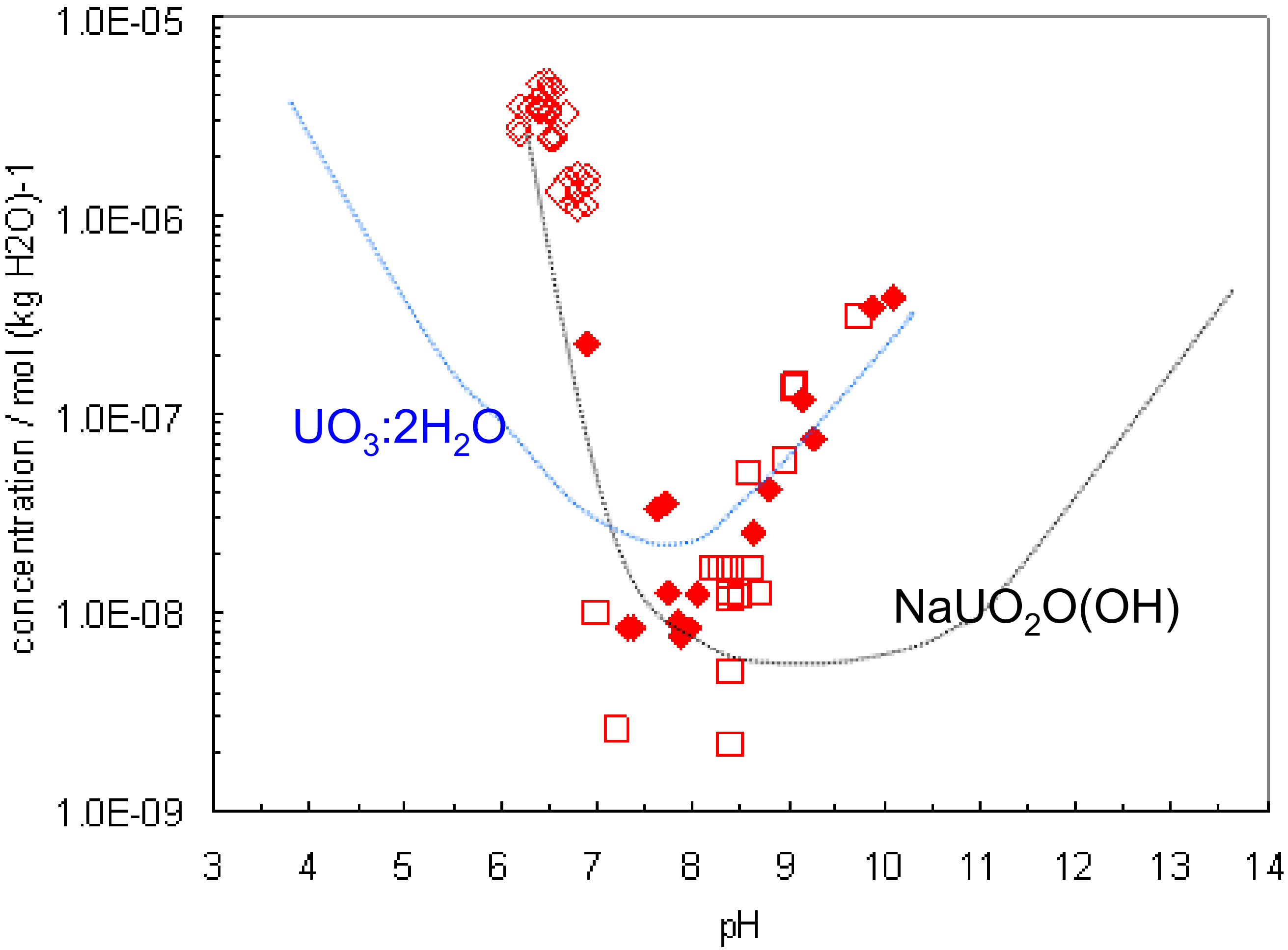




transformation into $NaUO_2O(OH)$

Altmaier, M. et al., Solubility of U(VI) in NaCl and MgCl2 solutions (in prep.)

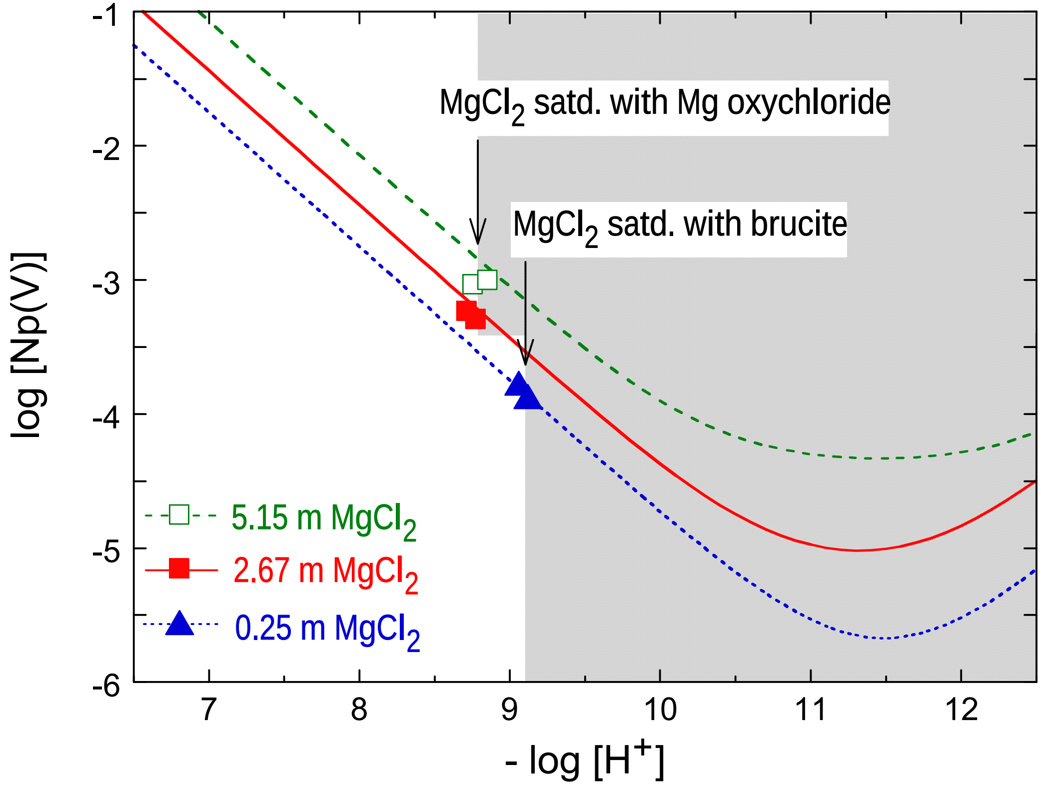
Comparing U concentrations in full-scale experiments to solubility of U(VI) phases



U(VI) concentration controlled by solubility of schoepite – or – $NaUO_2O(OH)$

Np(V) solubility experiments

In full-scale experiments, 1*10^{-10} M Np measured after 9 years, increased to $8 \pm 4 \cdot 10^{-10}$ M after ~15 years – Np concentration far below NpO_2OH solubility

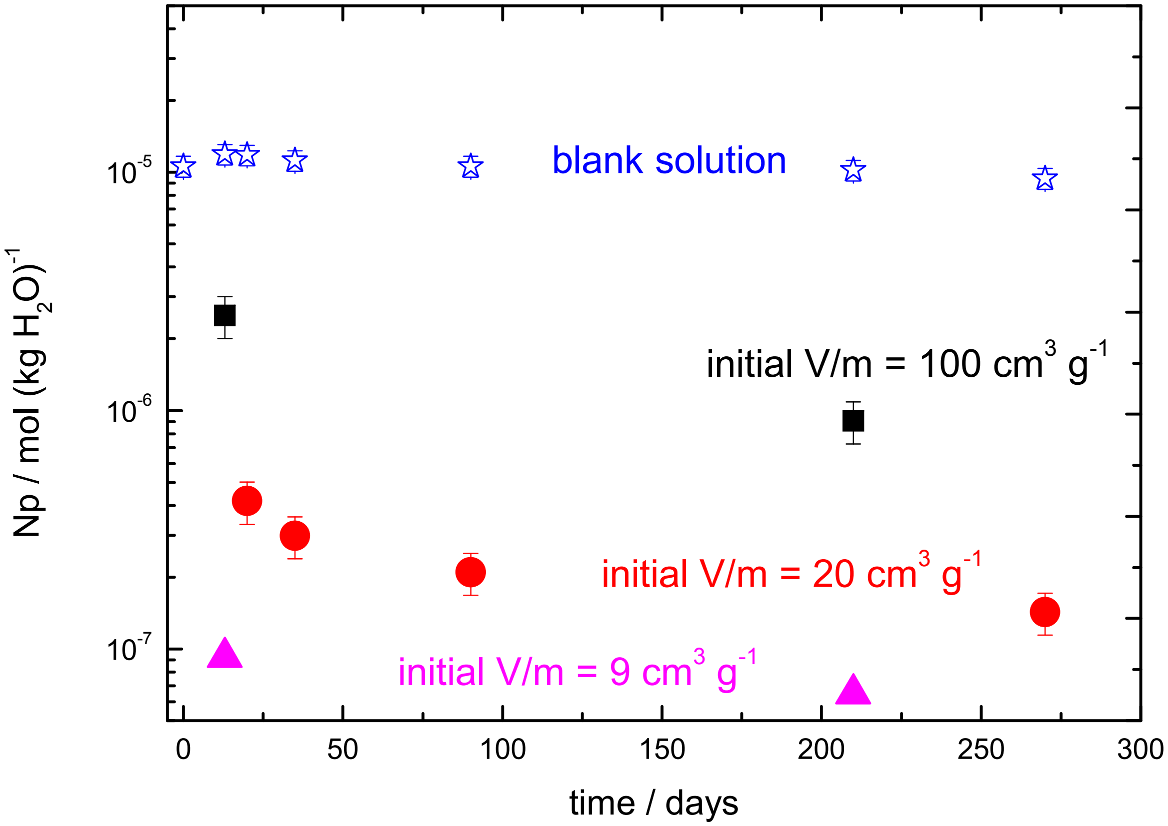


sorption phenomena
controlling Np
in full-scale experiments?

Neck, Altmaier, Müller, Metz, Kienzler (2003): FZK-INE 001/01

Np(V) sorption experiments: kinetics

- adding aliquots of ^{237}Np(V) stock solutions to equilibrated cement / Q-brine systems
- main mineral phases: Mg-oxychloride, hydrotalcite, gypsum
- sufficient inventory of equilibr. phases: same solution composition for changing V/m
- measured Np(V) concentrations, <10^{-6} M, far below NpO_2OH solubility

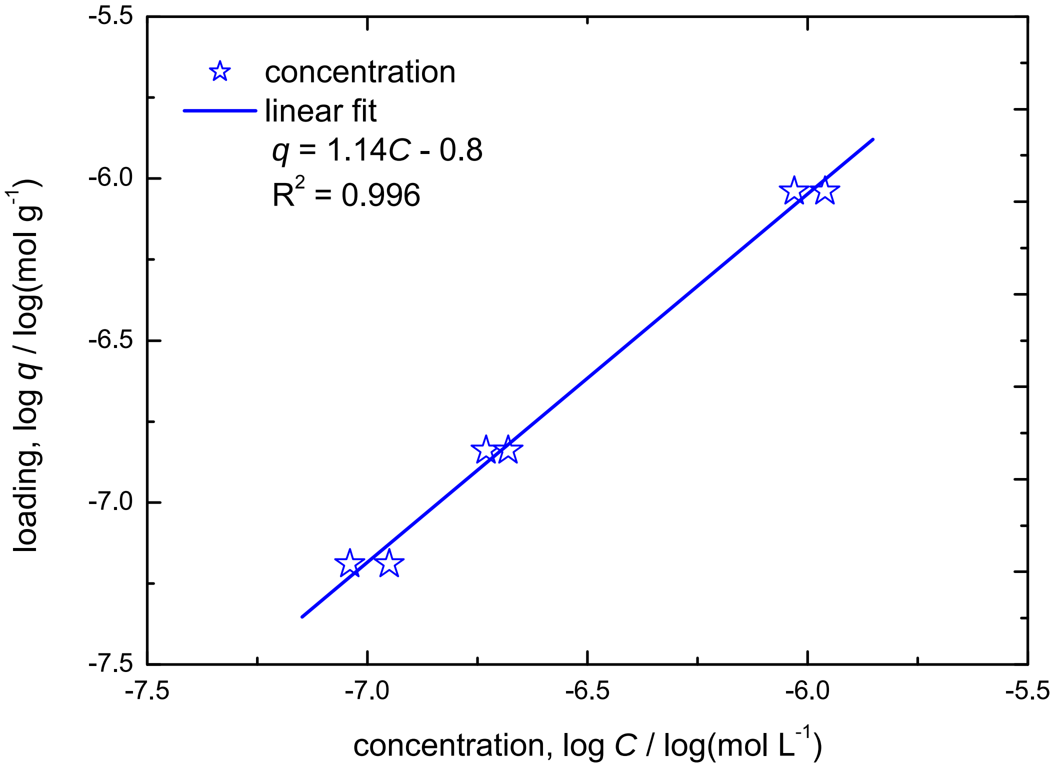


sorption equilibrium
approached after 50 days

Np(V) sorption experiments

results of equilibrated sorption experiments

linear isotherm derived from log (Np loading mol/g) vs. log (Np_{aq} mol/L) based on sorption coefficient, Np concentration in the full scale experiment is calculated to be $1.3 \pm 0.3 \cdot 10^{-9}$ M - compared to $8 \pm 4 \cdot 10^{-10}$ M measured after ~15 yrs.



Conclusions

Homogenous distribution of mineral phases in corroded cement blocks – and - formation of stable phases (hydrotalcite, gypsum, halite, brucite +/- Mg-oxychloride) indicate equilibration of cement / brine full-scale experiments within ~25 years

Simulated evolution of $MgCl_2$-brine / cement system as a function of corrosion progress is found to be in fair agreement with results of full scale experiments and laboratory experiments

Due to high U inventory of the full scale experiments, U concentrations in solution aliquots correspond to calculated solubilities of schoepite / NaUO2O(OH)(s)

Observations suggest that Np retention is controlled by adsorption onto cement corrosion products rather than by solubility phenomena

Waste components (nitrate, oxalate …) do not affect significantly geochemical evolution / behaviour of Np, U

Outlook

Open Post-Doc Position
Interactions of radionuclides with cement corrosion products
Contact: Volker Metz <volker.metz@kit.edu>

TRePro II 2009
Workshop on Modelling of Coupled Transport Reaction Processes
Karlsruhe, Germany, March 18 - 19, 2009
Contact: Johannes Lützenkirchen <johannes@ine.fzk.de>

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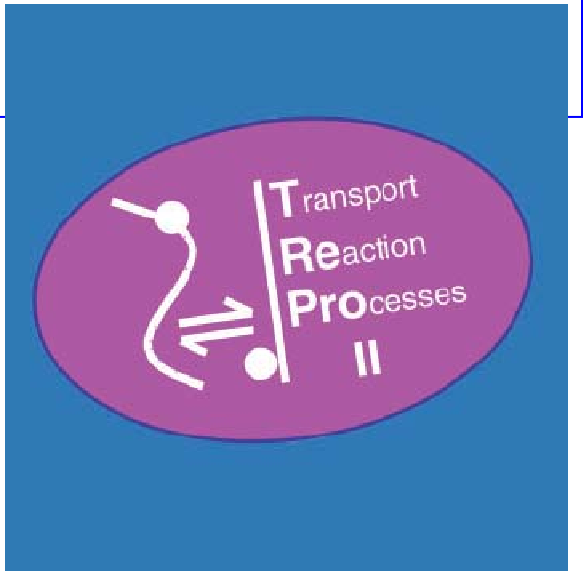


Thanks for your attention!

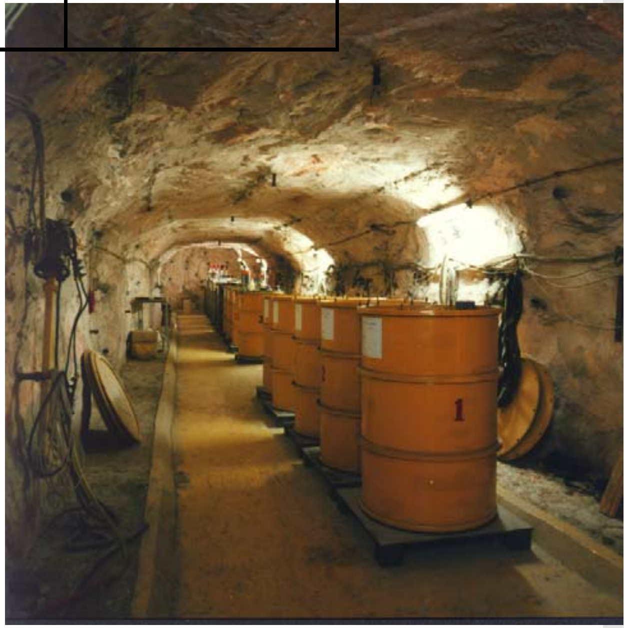
Txt

Experimental systems

sample	doping	water/cement ratio	leachant	start of leaching	termination (drilling)
#25	U(nat)	0.3	Q-brine	1984	
#26	U(nat)	0.34	Q-brine	1984	
#28	Cs-137	0.43	Q-brine	1984	2006
#33	U(nat)	0.5	Q-brine	1989	2006
#34	U(nat)	0.5	Q-brine	1989	
#35	Np-237	0.5	NaCl-brine	1989	
#36	Np-237	0.5	Q-brine	1989	

320 – 340 kg cement forms with ^{237}Np 11 Bq/g, U$_{nat}$ ~15 Bq/g, ^{137}Cs 550 Bq/g

- periodical solution sampling - monitoring aqueous phase
- analyzing surface precipitates
- after approaching steady state (with respect to solution composition) termination & core drilling - solid sampling
- ^{137}Cs doped sample: evolution cement / brine system

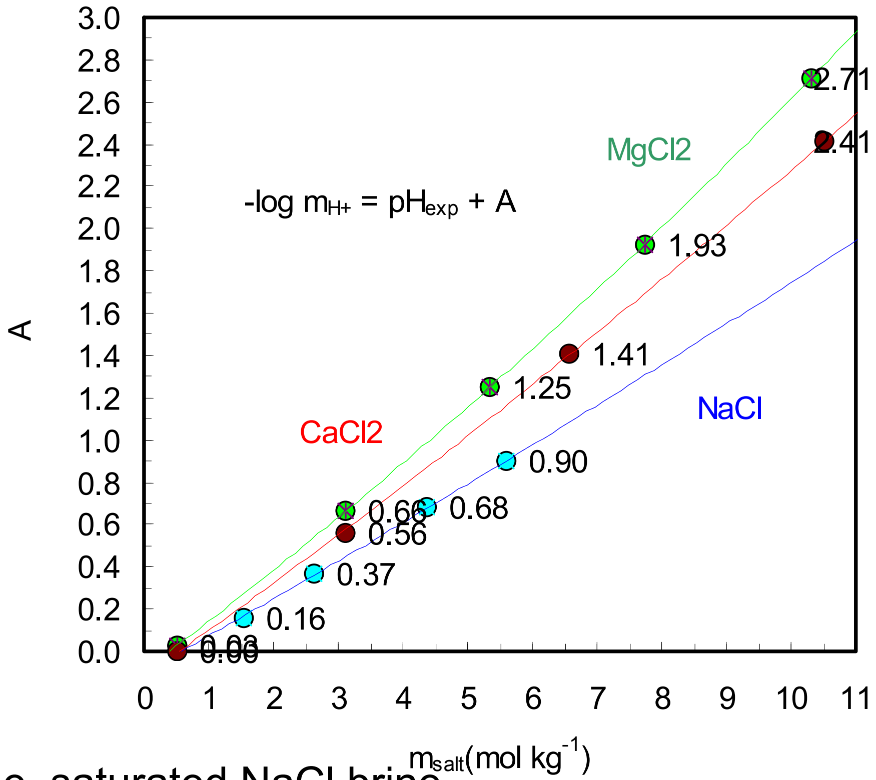


Comparison pH_{exp} with pH_{Pitzer} / $-\log m_{H+}$

$$pH_{exp} = pH_{Pitzer} - \Delta pH = -\log m_{H+} - A$$

Pitzer (EQ3/6) convention: $\psi_{Cl-/Cl-/H+} = \psi_{/Cl-/H+/H+} = \theta_{Cl-/Cl-} = \theta_{H+/H+} = 0$

$$\log(\gamma_{H+})_{Pitzer} = \log(\gamma_{Cl-})_{Pitzer} = 2\log(\gamma_{\pm})_{HCl}$$



Grambow & Müller: Q-brine, saturated NaCl brine

Altmaier, Neck & Müller: NaCl, $MgCl_2$, $CaCl_2$ 0.1 – 5.5 m and mixed $(Na_2,Mg,Ca)Cl_2$ brines

Application of Results

Low- and intermediate-level radwaste forms (LLW / ILW) emplaced in Zechstein diapirs, e.g. Asse salt mine (Germany):

- ≈1300 drums ILW
- ≈125000 drums LLW
- ≈10^{15} Bq total RN inventory (mainly Pu, U, Th, Cm, Np and Cs)
- intrusion of $MgCl_2$-rich Q-brine
- >30000 t Portland cement (OPC)
- ≈ 65000 m^3 void volume

interaction of actinides with cement corrosion products critical for the long-term safety of emplaced radwaste