

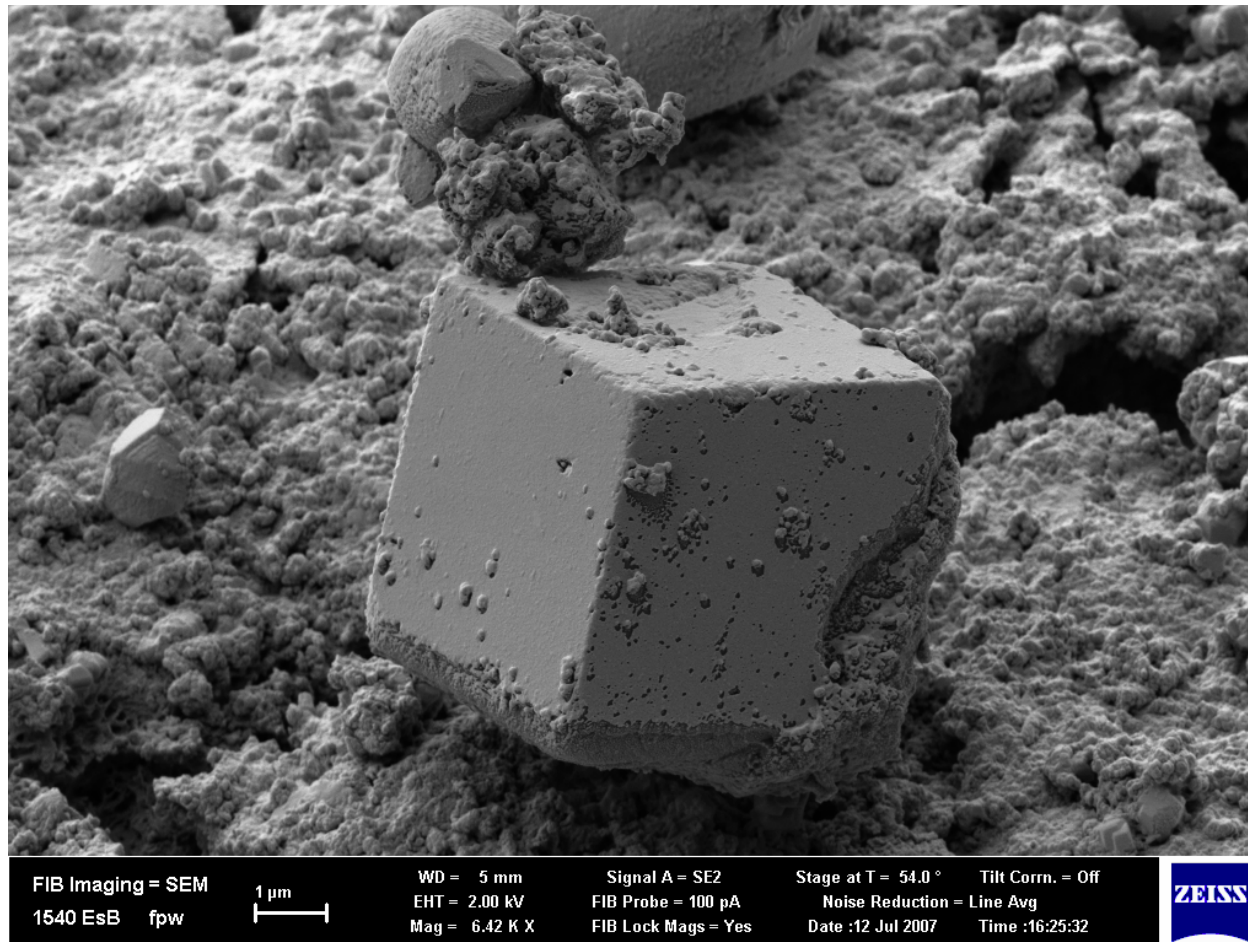
CEMENT-BASED MATERIALS IN CONTACT WITH WATER – REACTIVE TRANSPORT DRIVEN BY SURFACE PROCESSES –

M. Schwotzer¹, T. Scherer², A. Gerdes^{1,3}

¹ Forschungszentrum Karlsruhe, ITC-WGT

² Forschungszentrum Karlsruhe, INT

³ University of Applied Sciences-Karlsruhe



- Deterioration of cement based materials in tap water storage
- Experimental investigation of reaction mechanisms
 - Results
 - Model of the reaction mechanism
 - Validation on case studies
- Conclusions



Observations in tap water reservoirs

Deterioration of cement-based materials during service life in contact with hard tap water (in carbonic acid equilibria)

Appearance:

- brown spots
- strictly local
- sometimes arranged in regular patterns

Mechanical properties:

loss of strength



Observations in tap water reservoirs

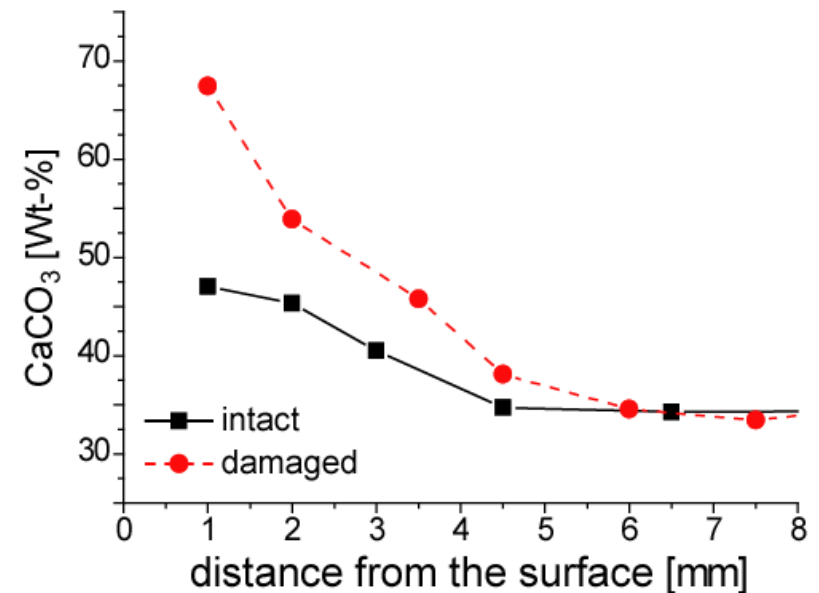
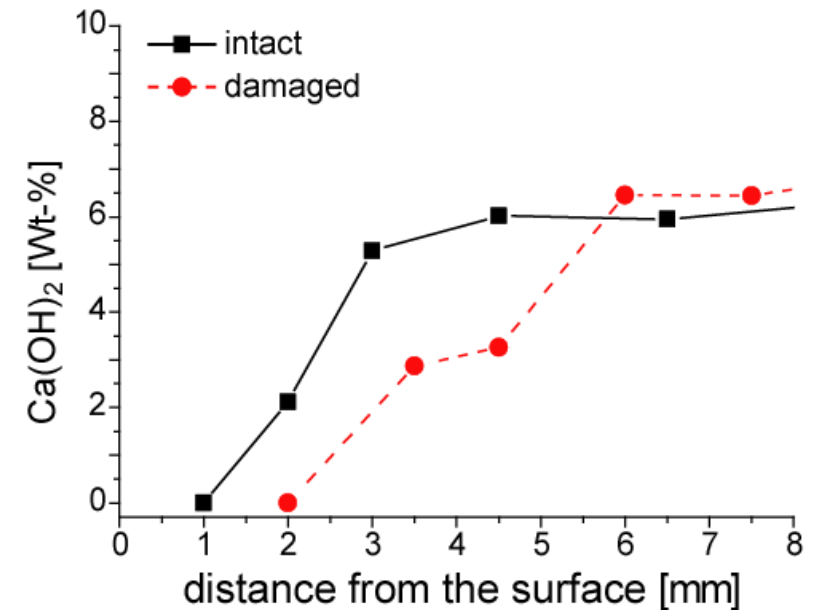
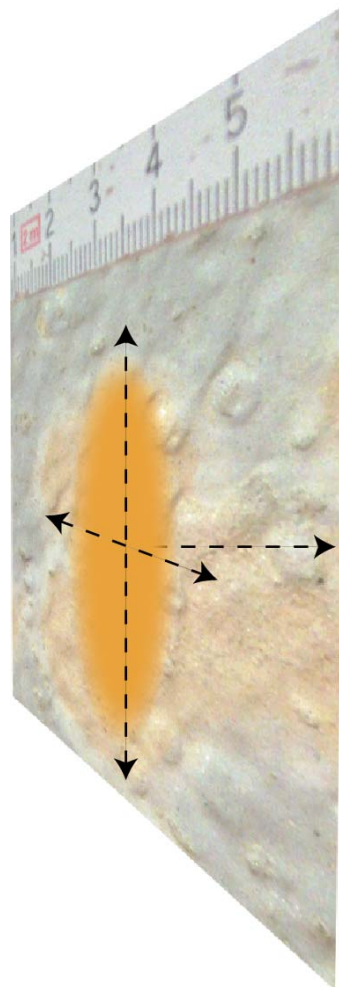
Chemistry:

- discharge of $\text{Ca}(\text{OH})_2$
- „intrusion“ of CaCO_3
- degradation of CSH

Kinetics:

Sometimes 6 months after application in permanent „contact“ with hard tap water: lateral- and depth-expansion of the damage

- Electrical fields ?
- Microbiology ?
- Acid cleaning agents ?
- Hydraulic changes during tap water reservoir use ?



Open questions...

Reactive transport:

Transport:

- Diffusion

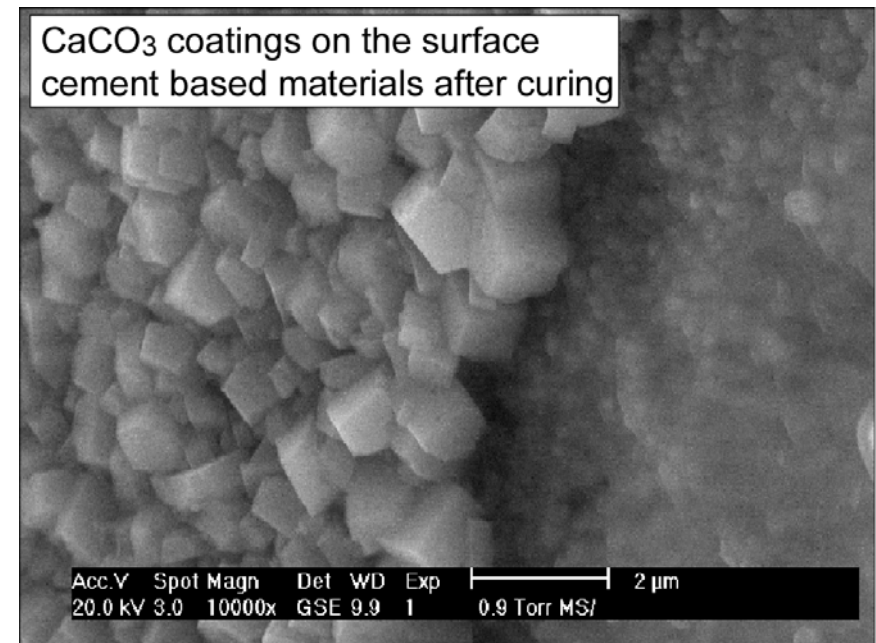
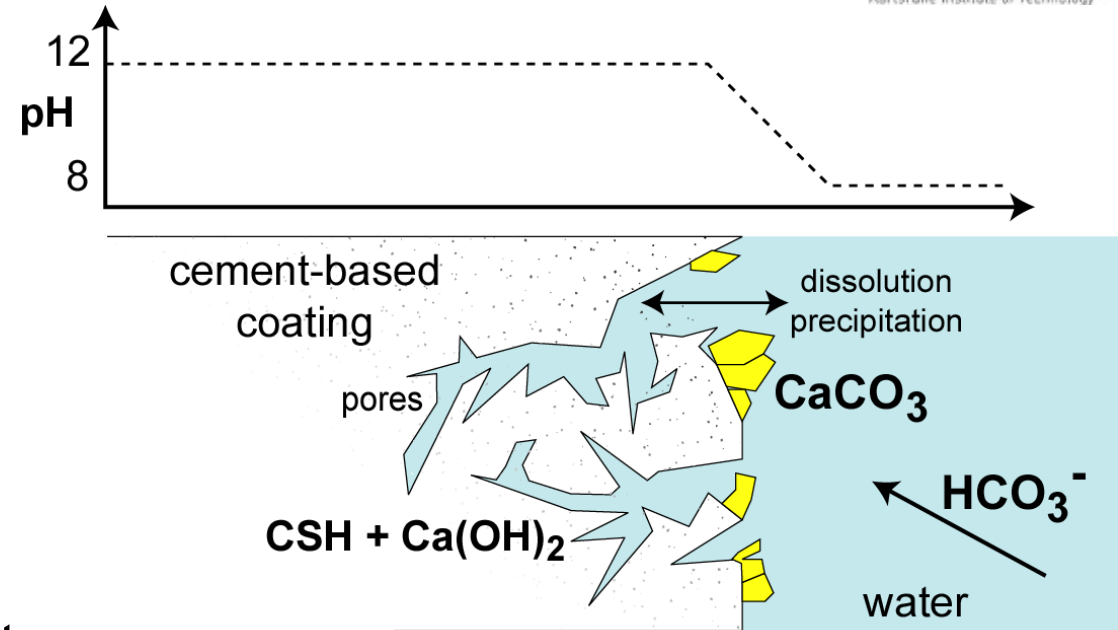
Chemical reactions:

- dissolution
- precipitation

Why does the „damage“ occur with cement-based materials in permanent contact with (hard) tap water?

What about a protection against leaching by CaCO_3 -layers?

Why do we observe such significant local differences in the velocity of reactive transport?



Focus	Experiment	Methods
Chemical reactions		
Material/water Interface	• Exposition of (fresh cut) cement paste surfaces	XRD, ESEM-EDX, FIB-ESB
Transport processes		
Material/water Interface	• Exposition cement paste samples	TG, MIP, ESEM-EDX
Material properties	• Accelerated transport by electrical fields – influence of the pore structure on reactive transport processes	TG, XRF MIP
Material properties	• Exposition experiments with commercial available mortars	ESEM, TG
Validation by case studies		
	• Characterisation of chemistry, mineralogy and structural properties (e.g. porosity and pore size distrib.) in case studies	XRD, TG, ESEM, FIB MIP

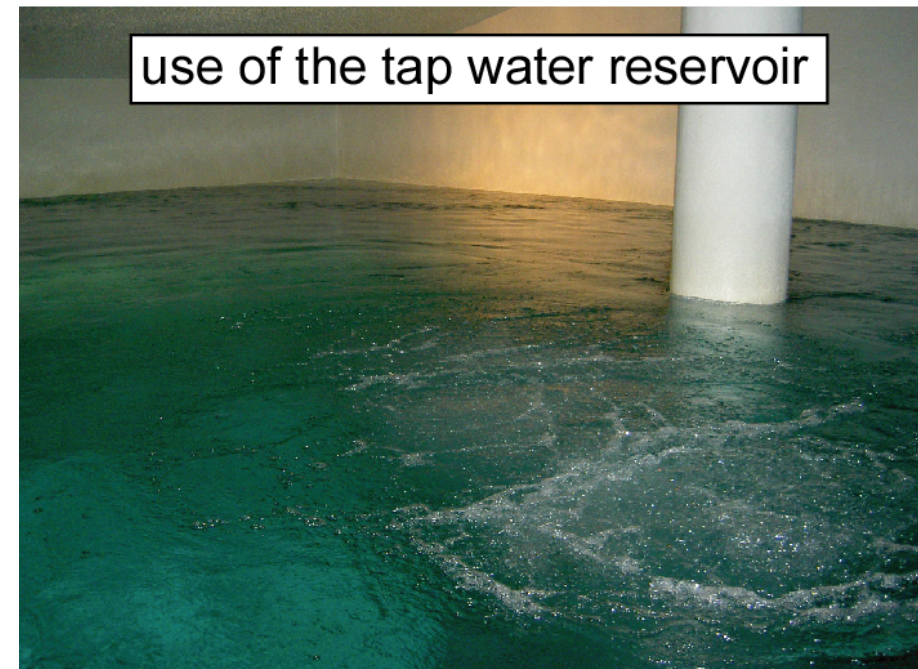
Construction phase:

- high humidity ($\sim 100\%$)
- low temperature ($\sim 10^\circ\text{C}$)

→ condensate formation can occur

Utilization:

- permanent in contact with tap water
- filling and emptying



Experimental setup

Experimental setup to characterize the cement paste/ water interaction, based on practical frame conditions

- Fresh cut slices (1 mm) of white cement paste ($w/c=0,4$)
- Temperature = 11°C

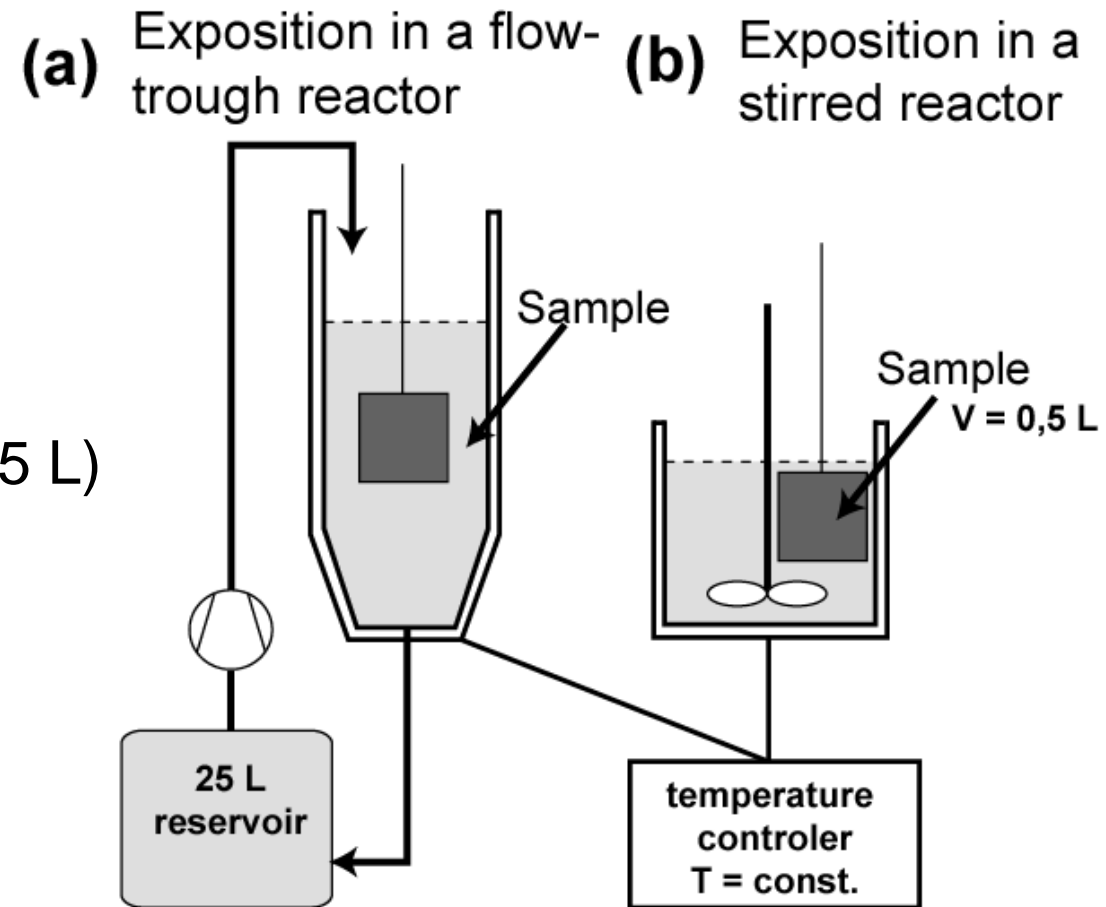
Different types of exposition:

Water

- demineralized water
- hard drinking water

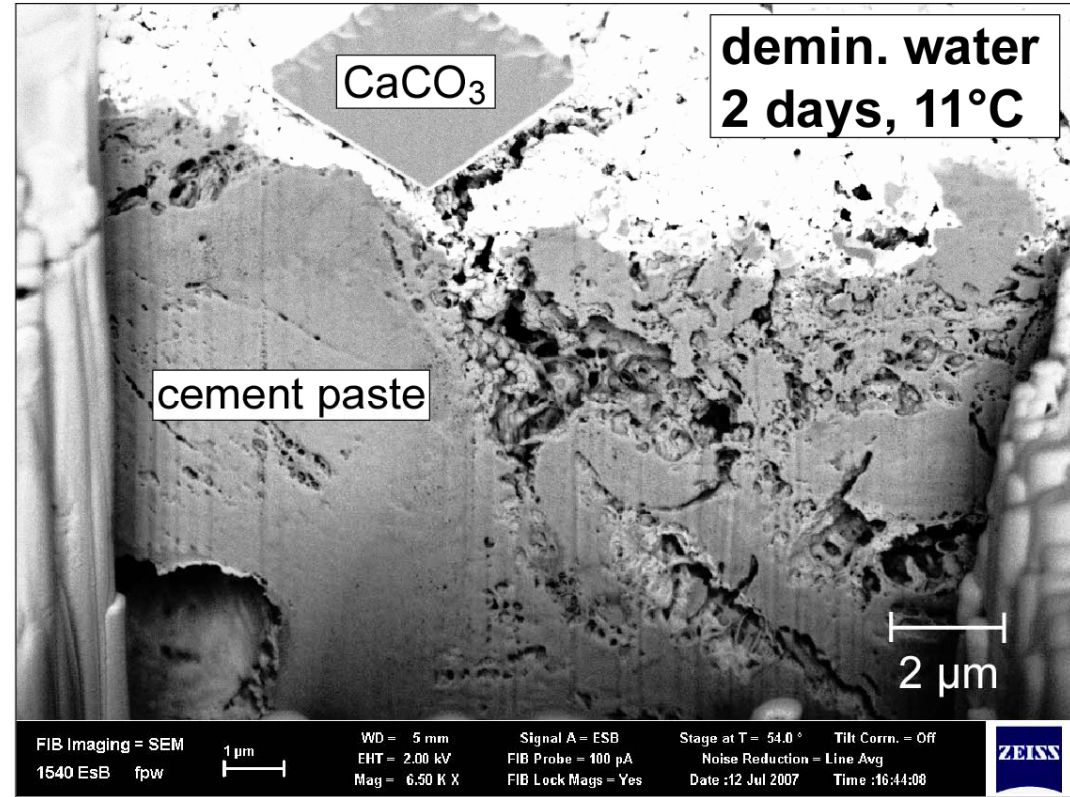
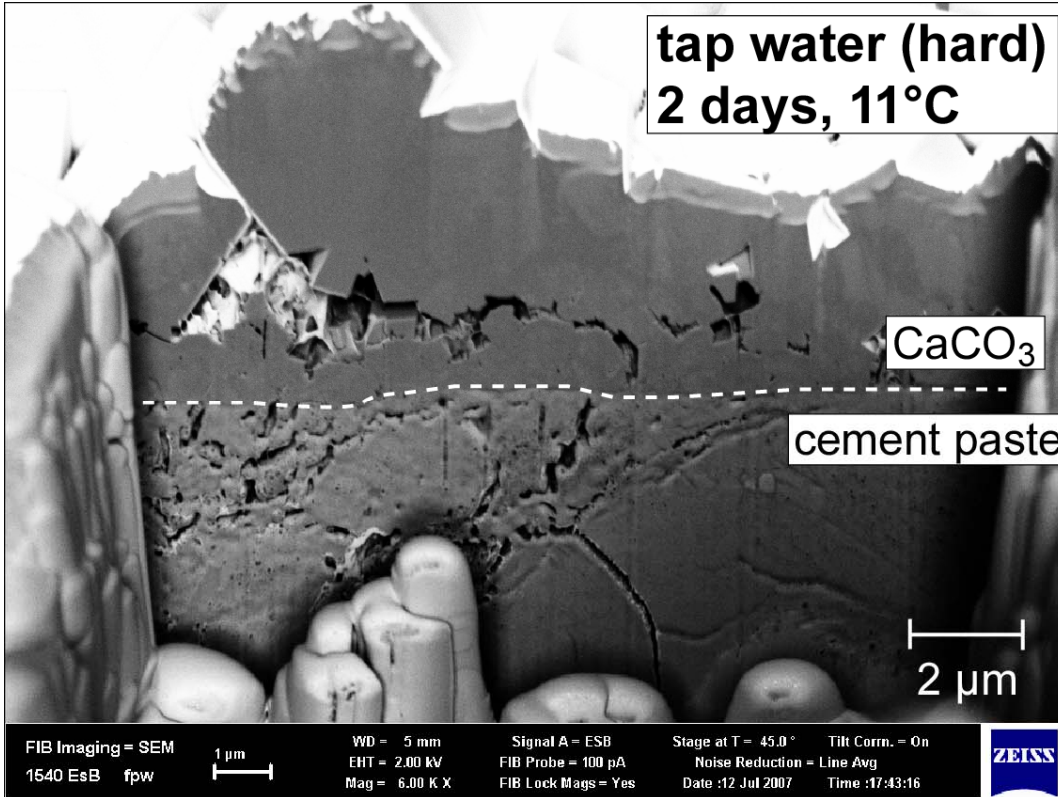
Basic conditions

- continuous water exchange ($V=25\text{ L}$)
- stirred ($V=0,5\text{ L}$), open system



What happens at the material/water interface?

Focused Ion Beam cuts



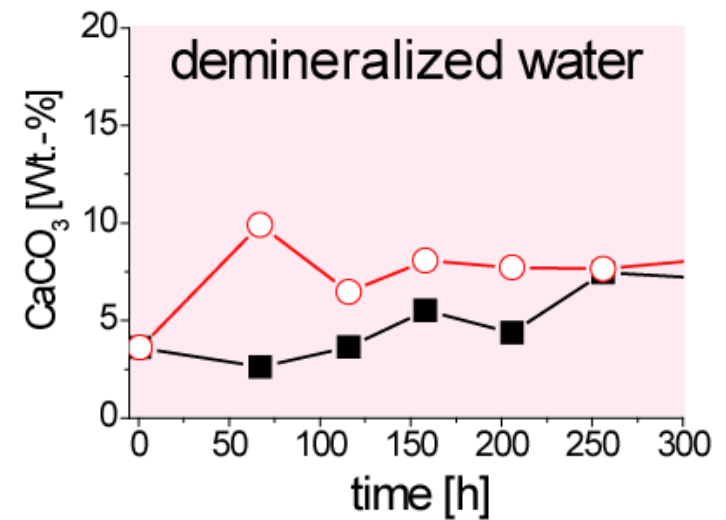
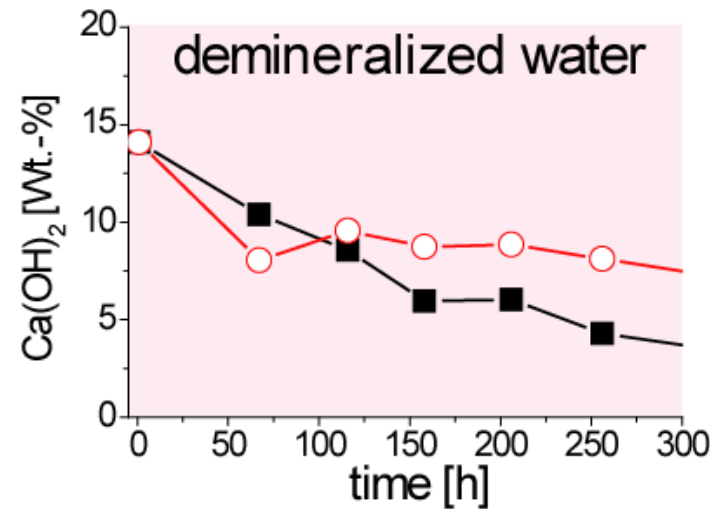
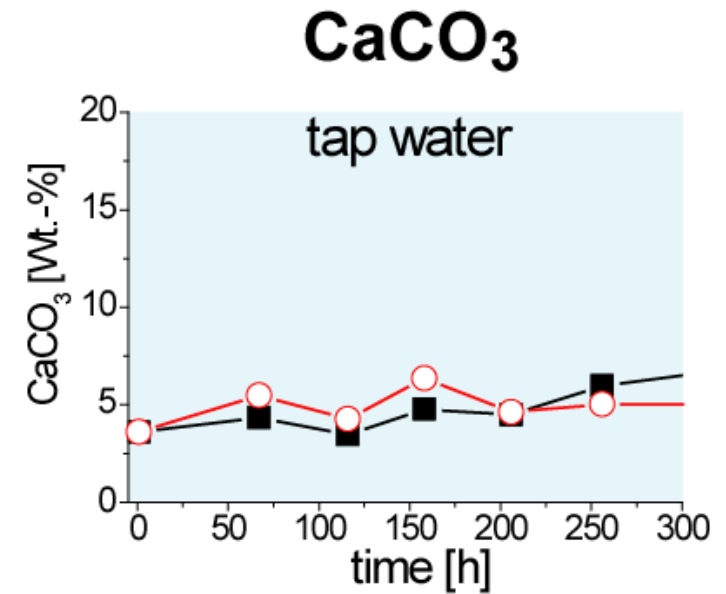
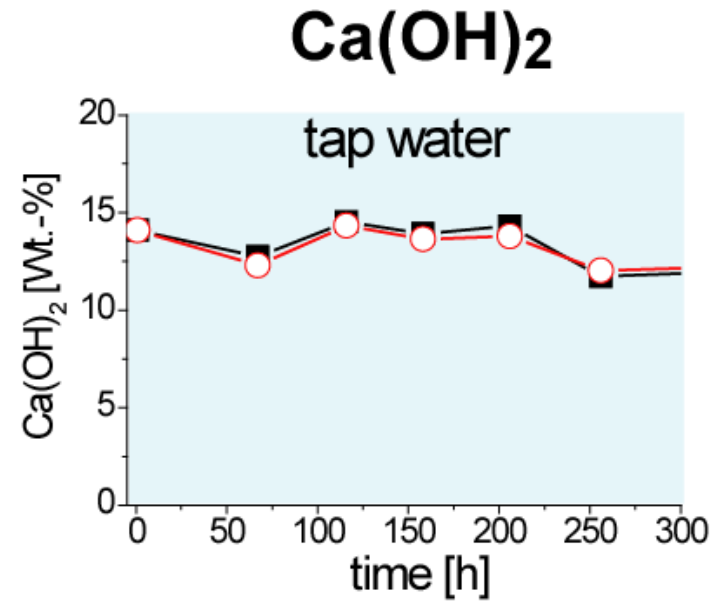
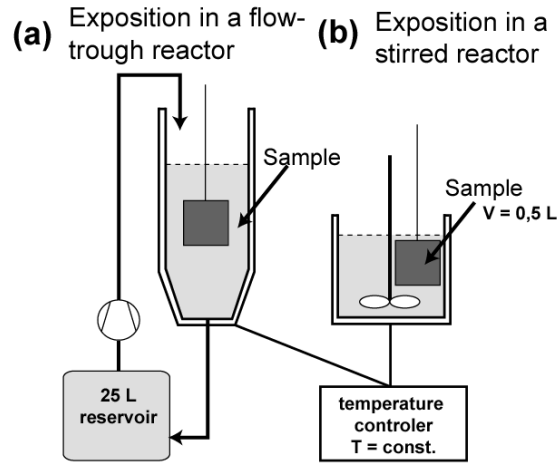
Contact with hard tap water:

- development of a covering CaCO₃-layer
- no significant impact on pore structure and chemical composition

Contact with demineralized water:

- No dense covering CaCO₃-crystallization
- Chemical attack on the cement paste
 - leaching
 - enlargement of the pore structure

Calcite and portlandite content vs. time



cont. water exchange, 25 L

 stirred, 0,5 L

Porosity and pore size distribution

Hard tap water:

no significant change in porosity and pore size distribution

Demineralized water:

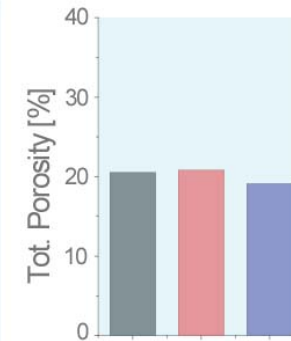
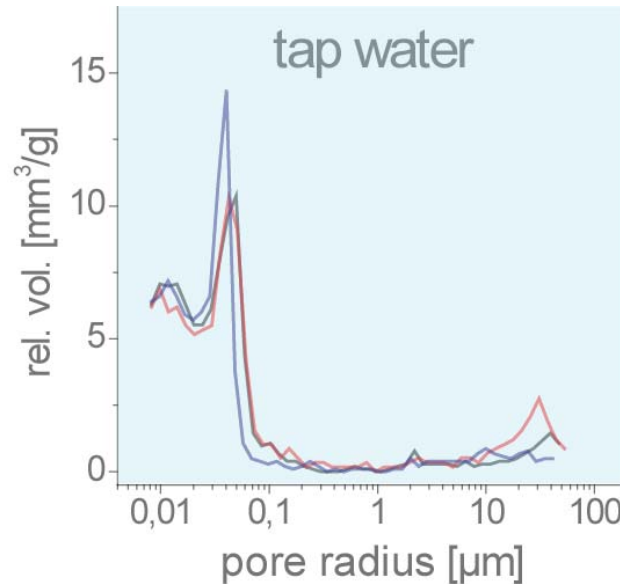
Increase of porosity and changes in pore size distribution

Increase in the smallest pore volumes

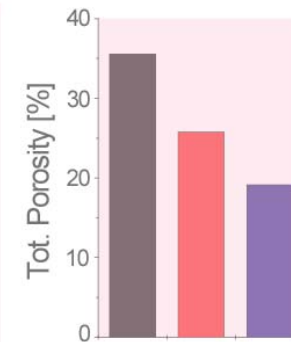
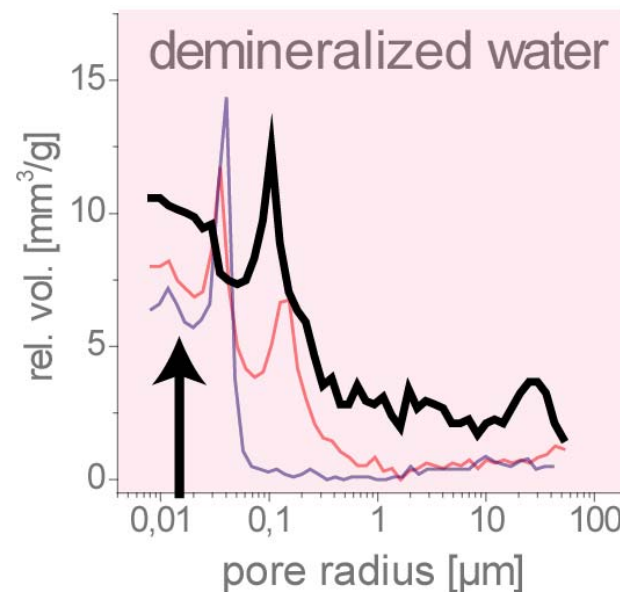
indicates that the paste is changing in ways other than just being destroyed, which would tend to decrease the surface area /fine structure.

(Thomas et al., 2004)

THOMAS J. J., CHEN J. J., ALLEN A. J., JENNINGS H. M. (2004): Effects of the decalcification on the microstructure and surface area of cement and tricalcium silicate pastes, *Cem. Concr. Res.*, **34**, 2297-2307



— cont. water exchange (25 L), 10 days
— stirred (0,5 L), 10 days
— reference



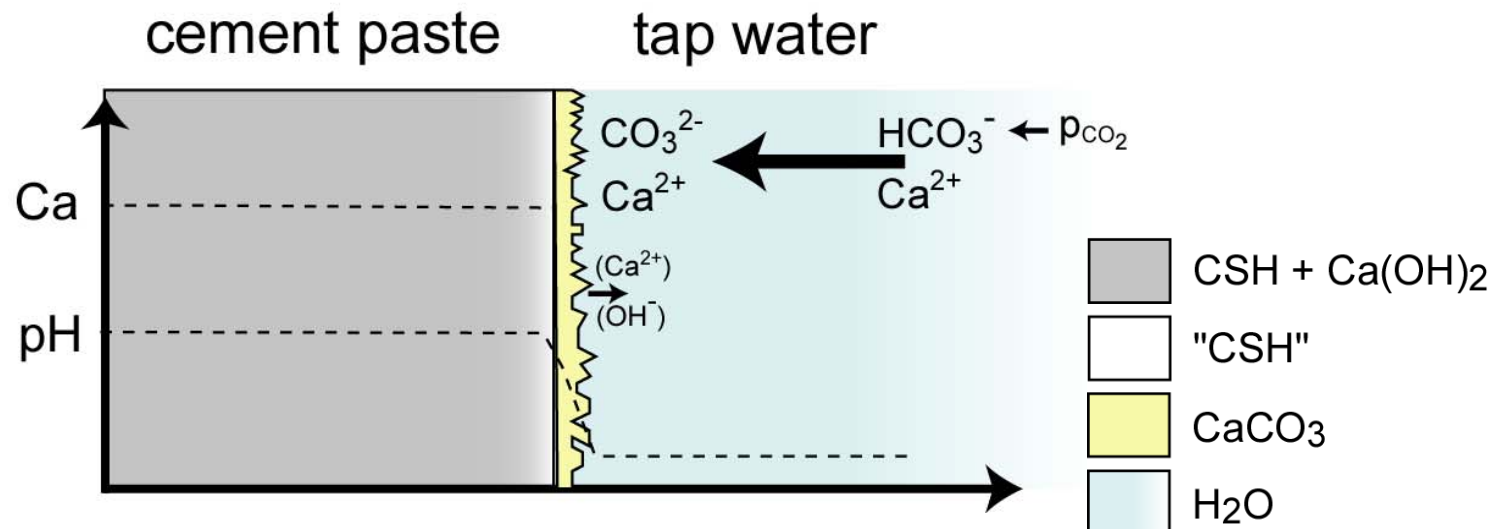
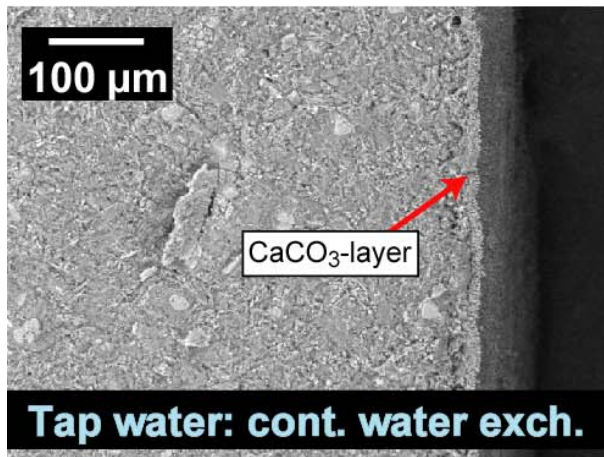
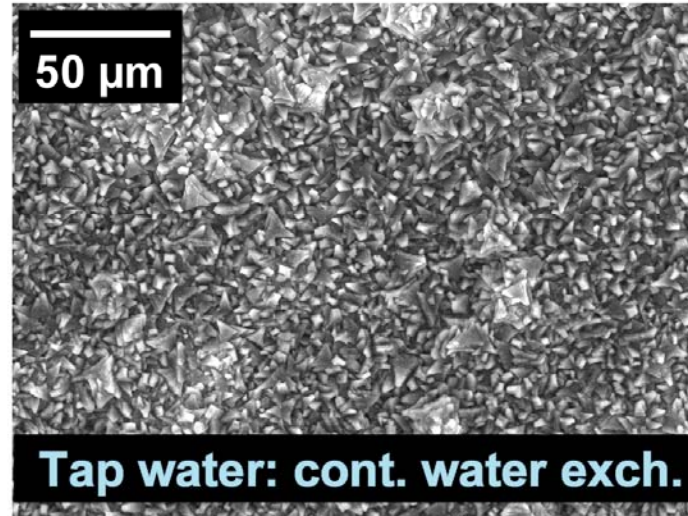
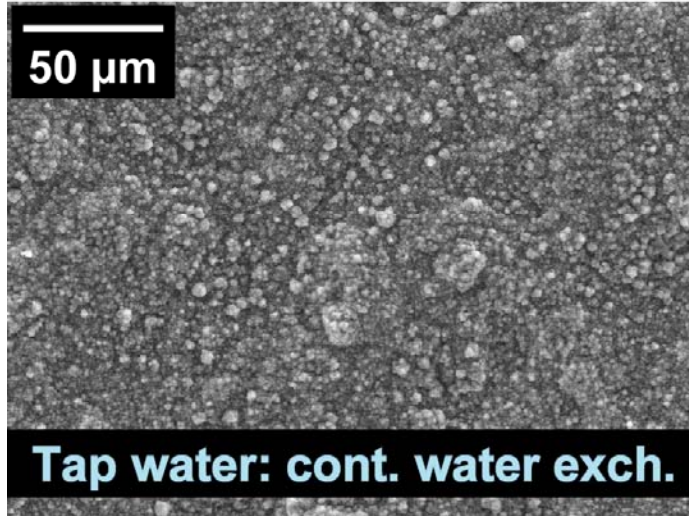
— cont. water exchange (25 L), 10 days
— stirred (0,5 L), 10 days
— reference

Surface processes in hard tap water

→ Cont. water exchange (25 L reservoir), tap Water: HCO_3^- available

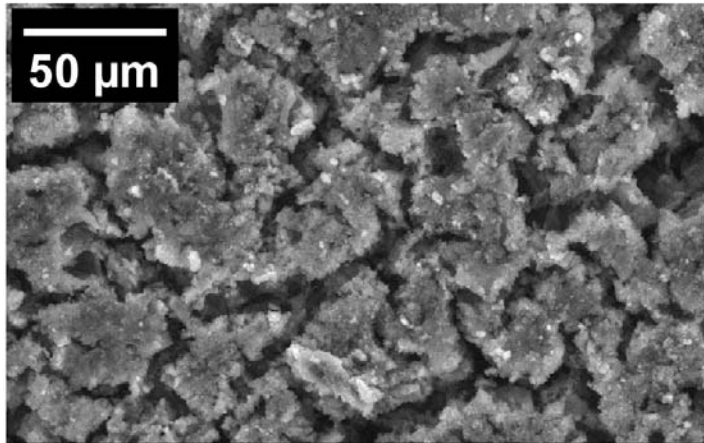
3 days

10 days

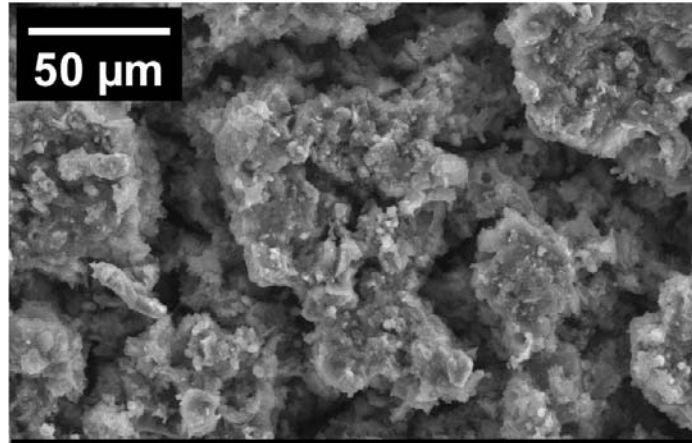


3 days

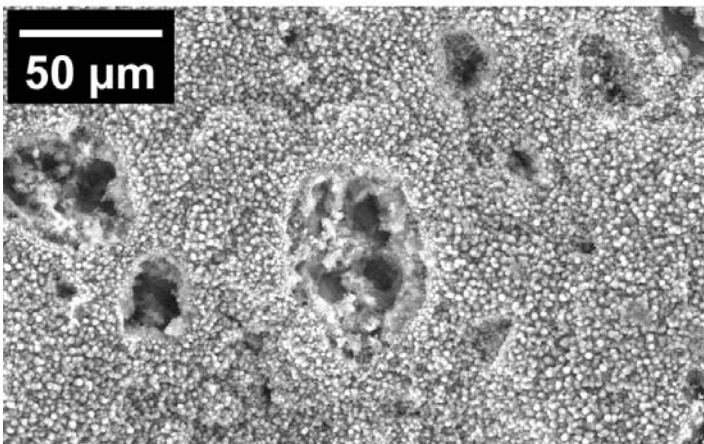
10 days



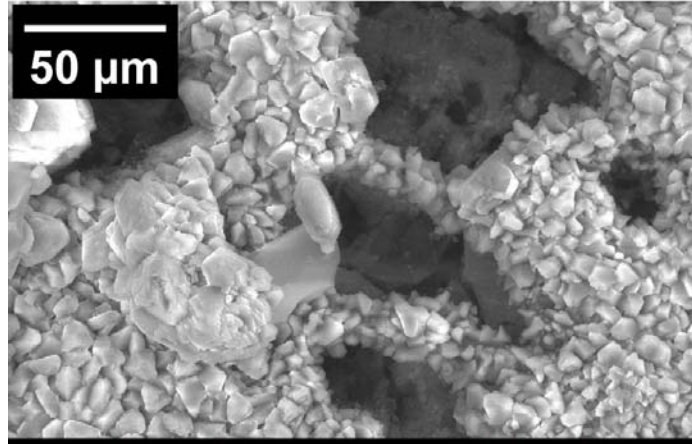
Demin. water: cont. water. ex.



Demin. water: cont. water. ex.



Demin. water: stirred



Demin. water: stirred

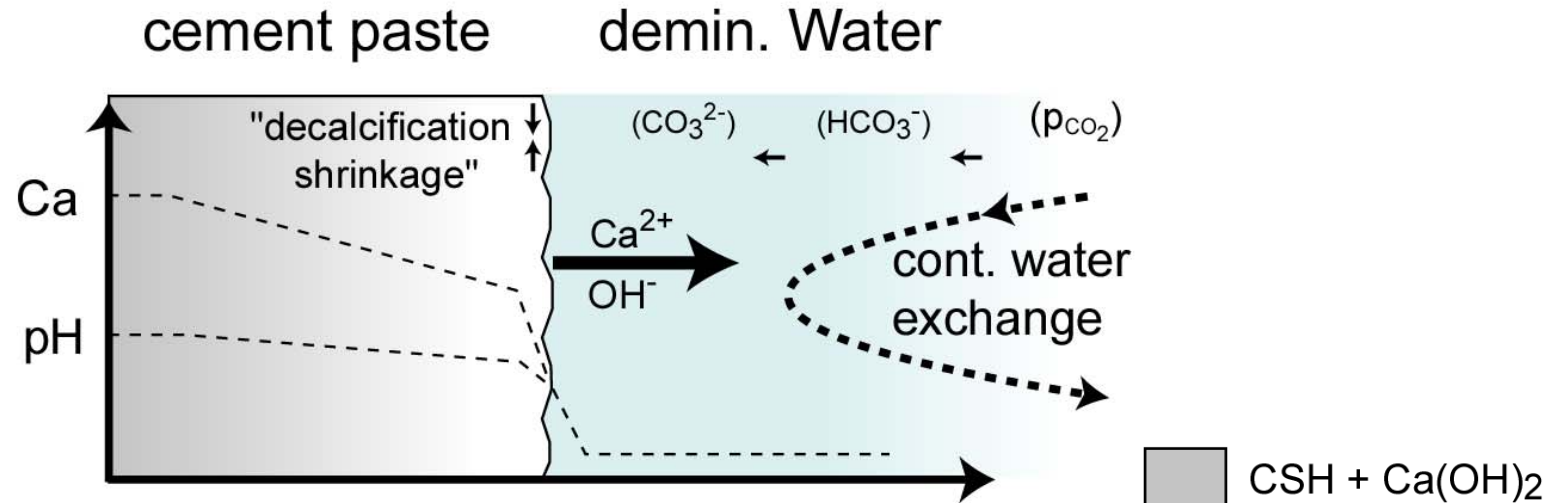
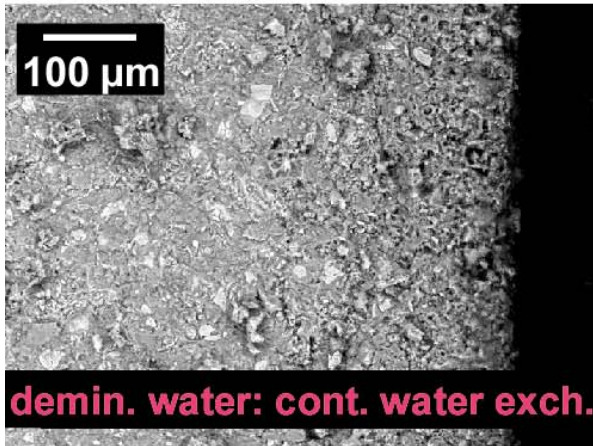
Demineralized water:

- Ca-leaching from the CSH-gel is associated with a decrease of volume
- „Decalcification shrinkage“ (Chen et al., 2006) leads to the formation of micro-cracks in the surface zone of the material
- In the stirred reactor: CaCO_3 overgrows the „leaching“ features

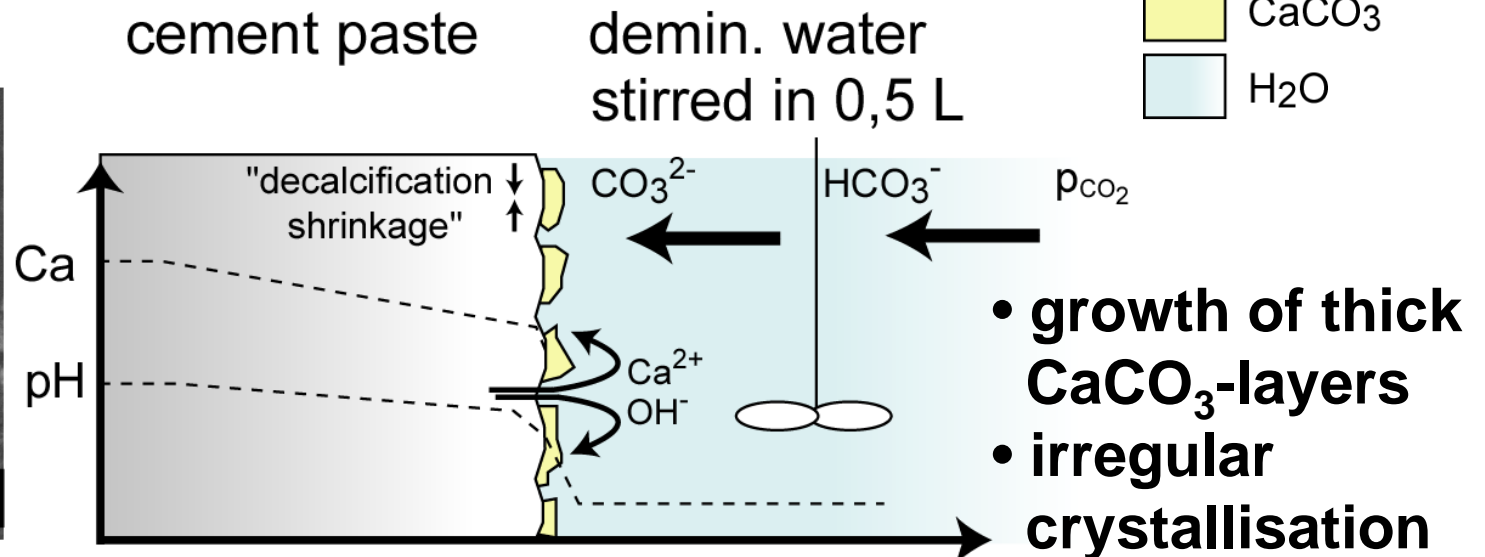
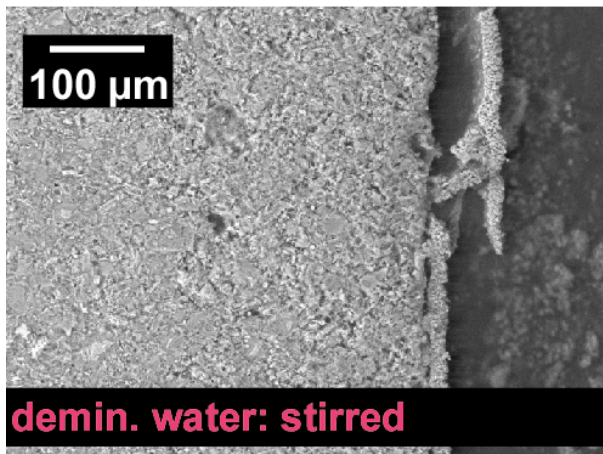
CHEN J. J., THOMAS J. J., JENNINGS H. M. (2006): Decalcification shrinkage of cement paste, Cem. Concr. Res., 36, 801-809

Reaction with demineralized water

→ Cont. water exch. (25 L reservoir), demineralized Water: **low CO₂ availability**

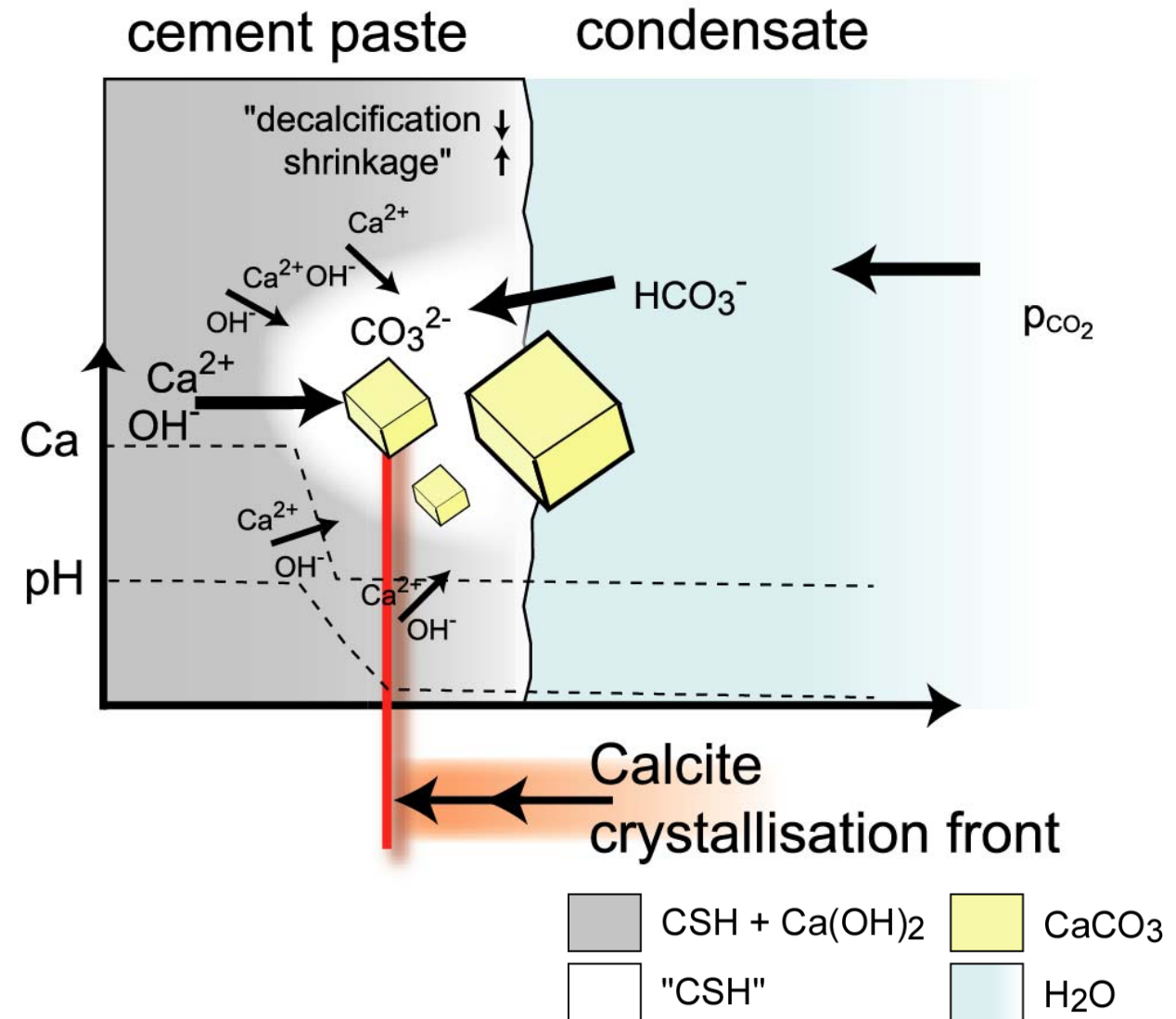
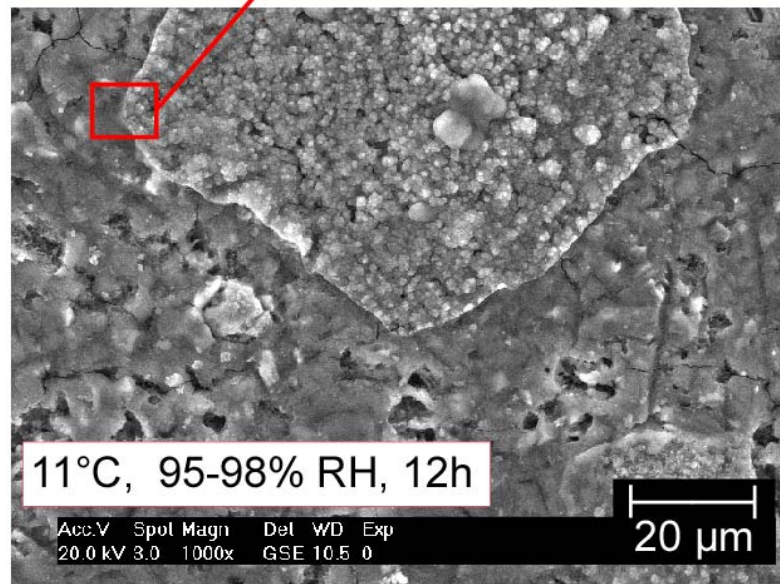
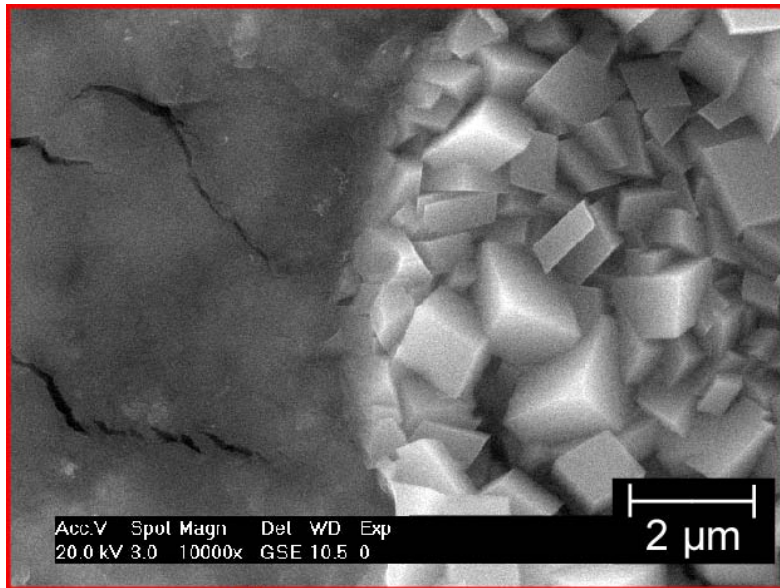


Stirred reactor (0,5 L) → **good CO₂ availability**



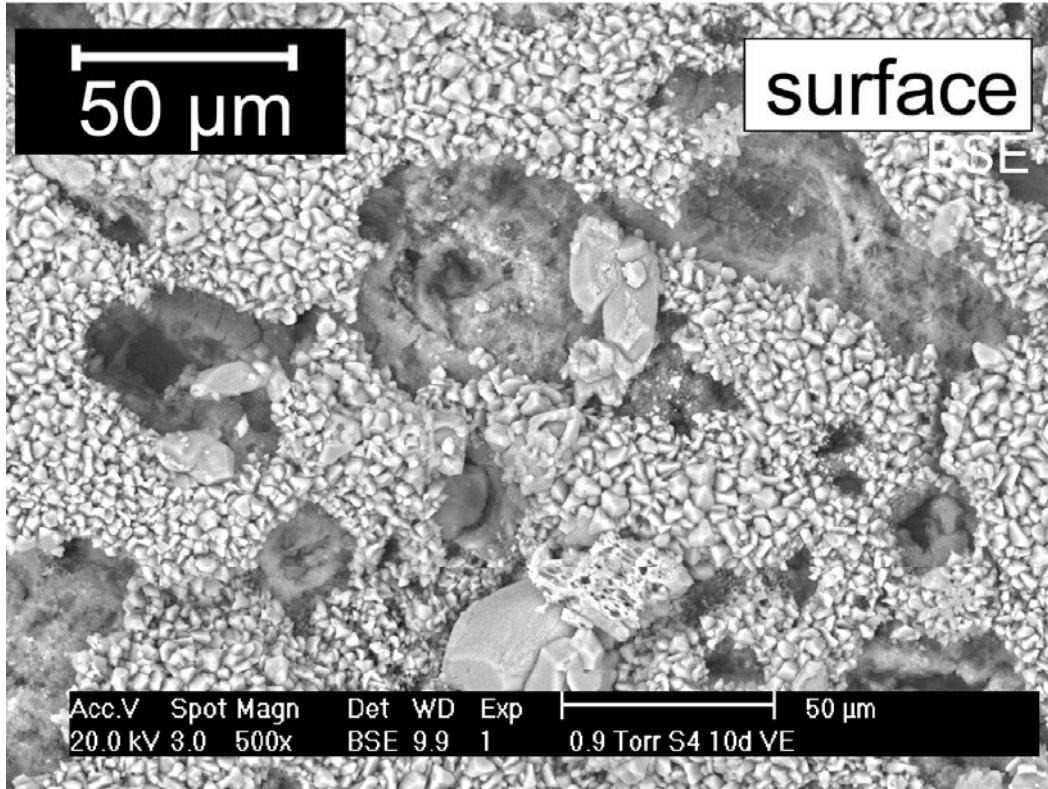
Step 1: Initial damage - material-condensate interaction

Local reaction under a condensate water drop:

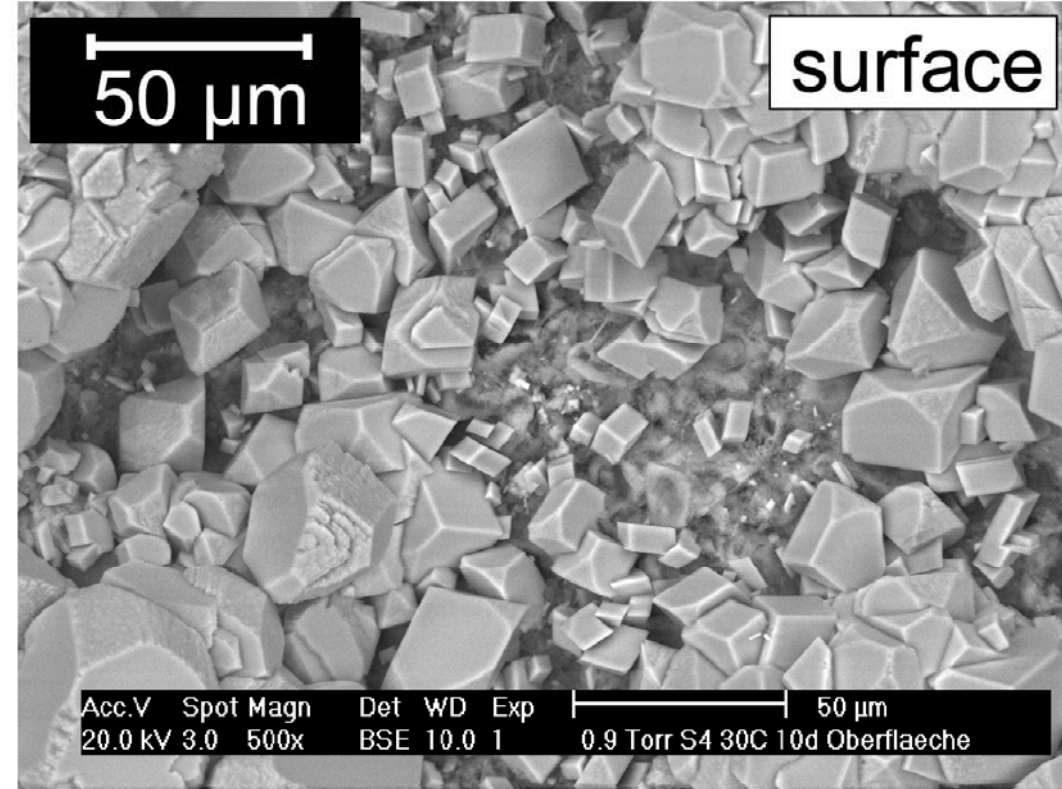


In this case, the CaCO_3 -layer has no efficient function as barrier against transport processes!

T=11°C

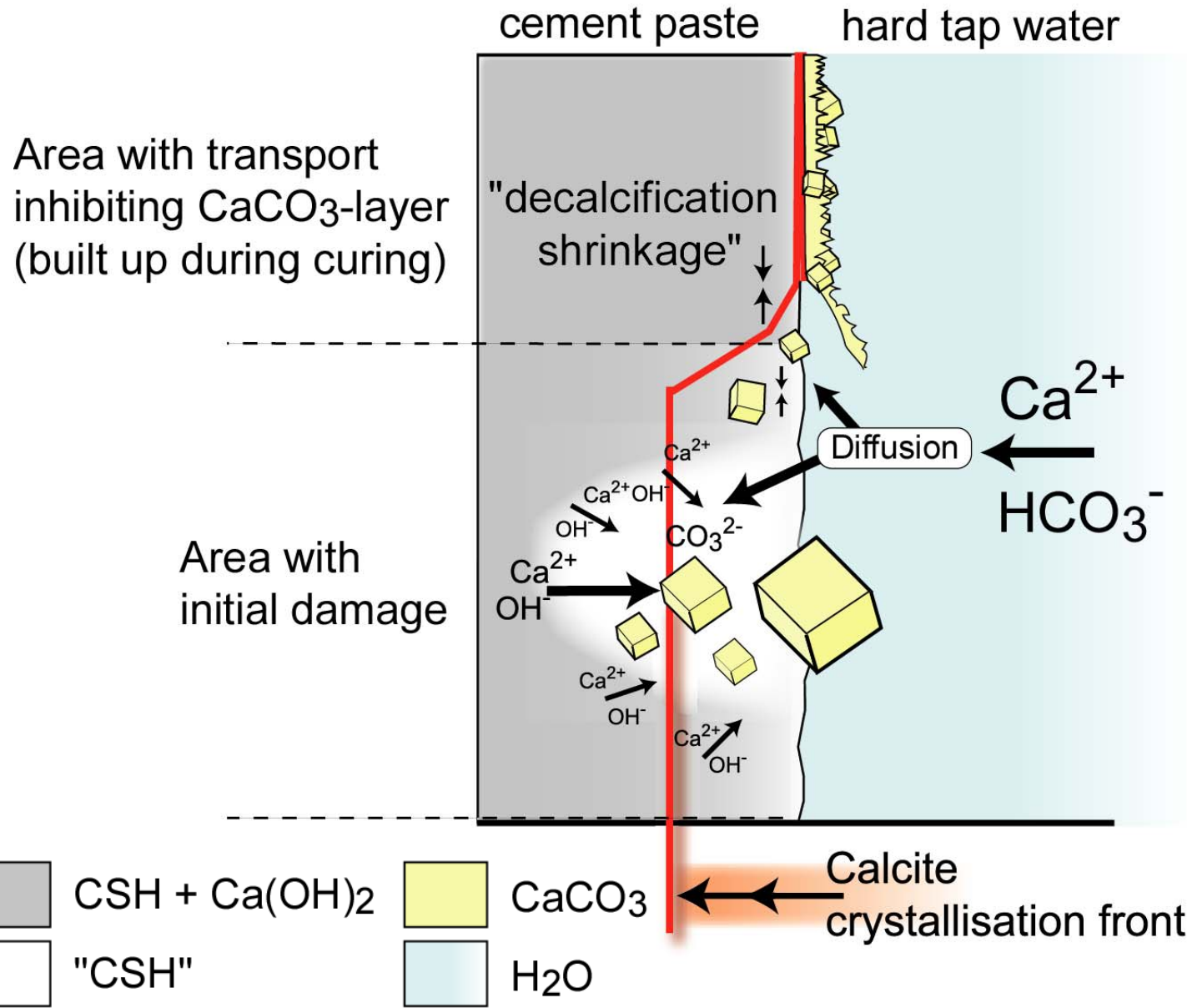


T=30°C



WPC paste $w/c=0.4$, 10 days stirred in demineralized water (0.5 L reactor)

Step 2: further reaction in contact with hard tap water



Consequence: lateral- and depth-expansion of the damaged areas

(1) Initial damage by reaction with condensate

- solution of CO₂ of in the condensate
- Surface crystallisation triggers further reactive transport
- Structural changes support the progression of the reaction in deeper areas

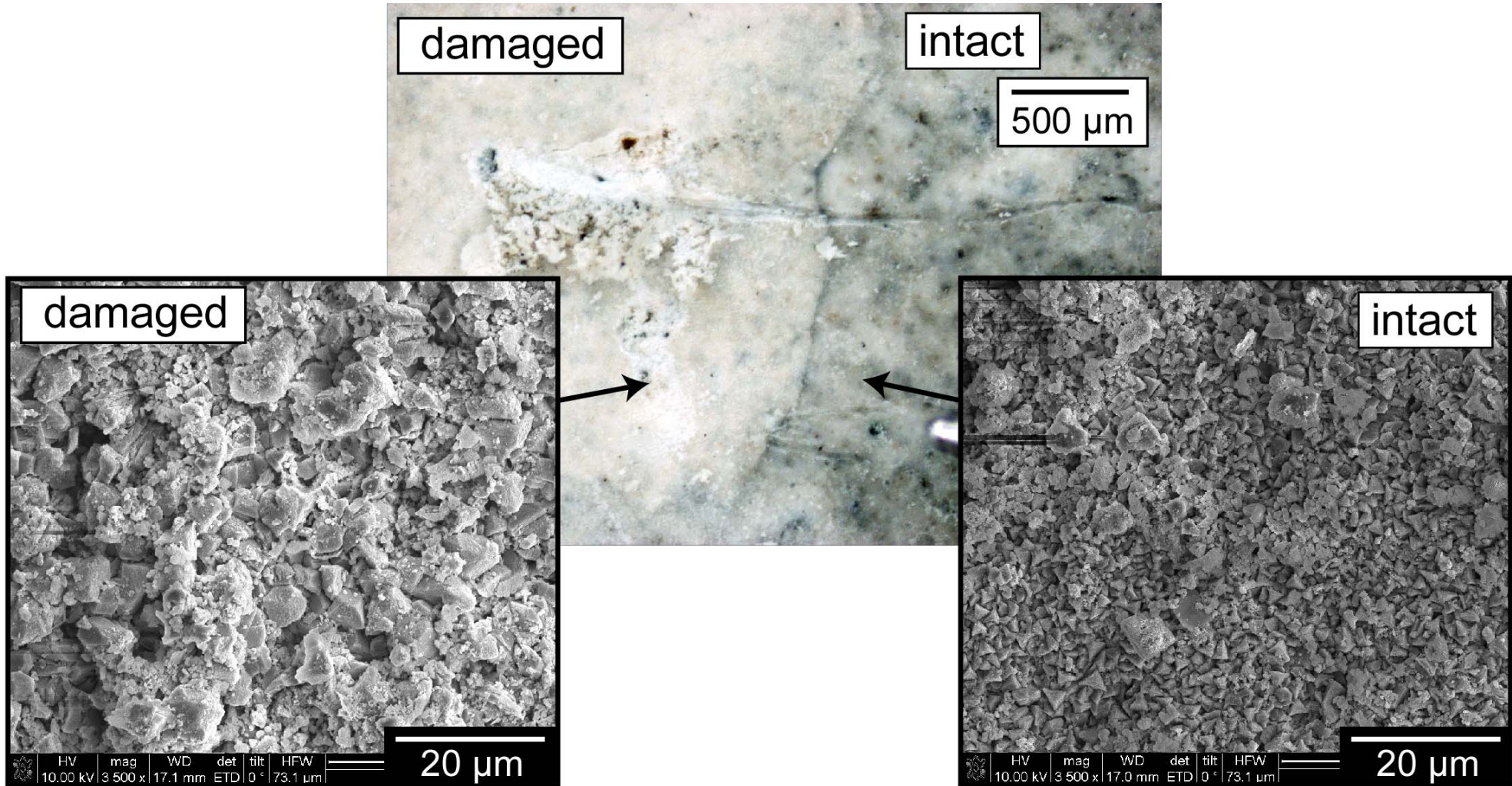
(2) Progress of the damage during contact with hard tap water

- Crystallisation front progresses in the depth
- „Decalcification shrinkage“ promotes the lateral development of the damage

Case Study: Interface material/water

What happens in the surface near μ -meters?

Focused Ion Beam preparation of a deteriorated area (white) and an intact area (gray)

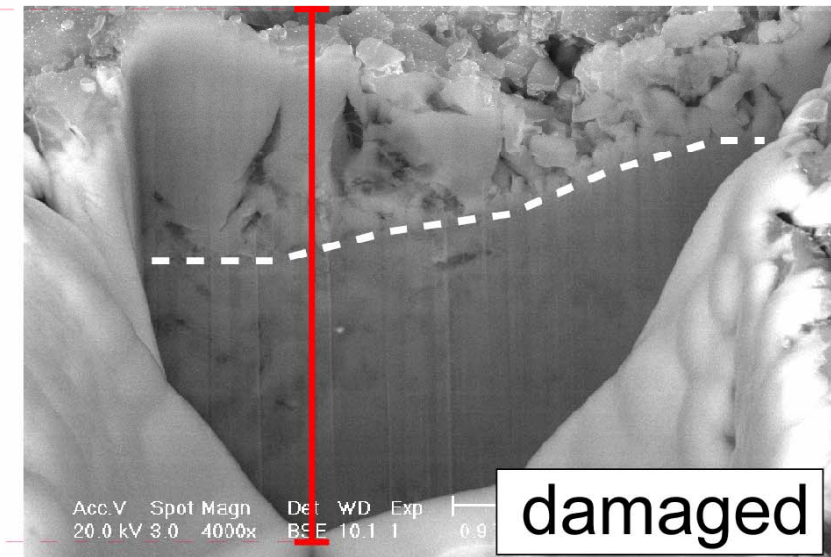
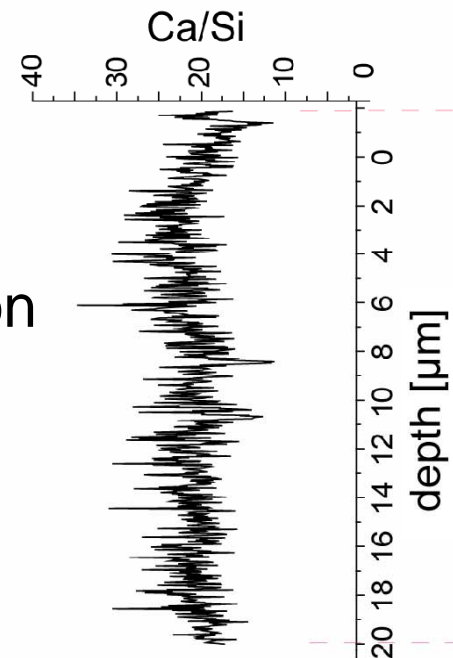
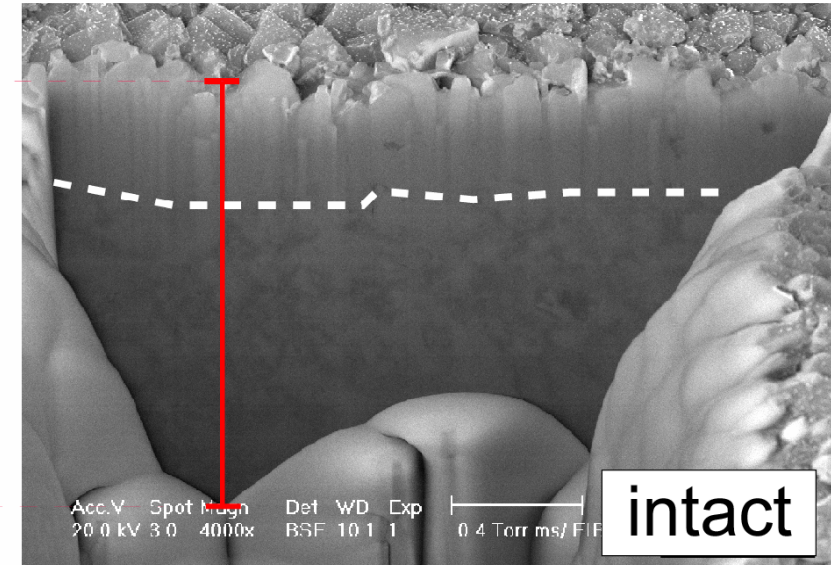
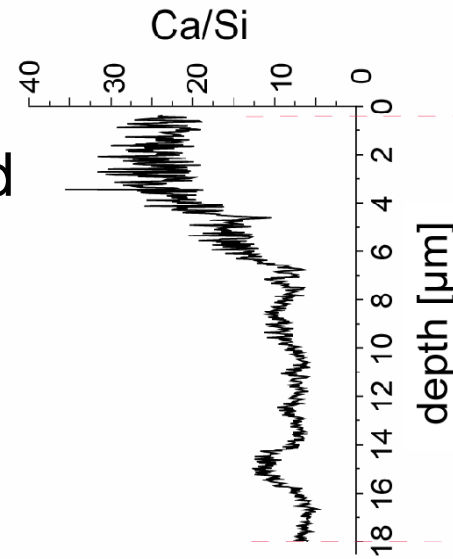


Case study: Interface material/water

EDX-analysis on FIB-cuts
in the surface of a damaged and
a intact mortar surface

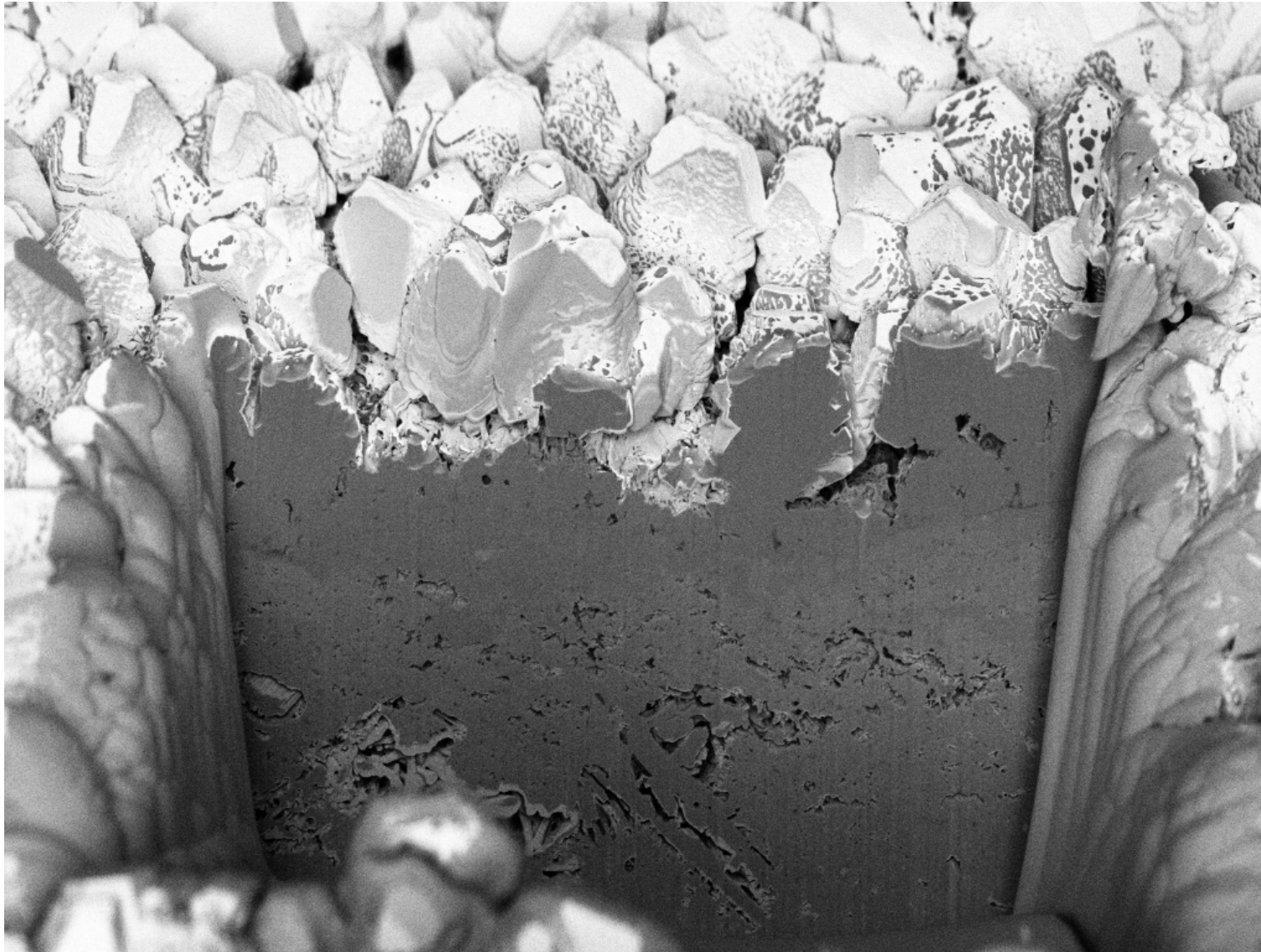
- **Structure of CaCO_3 layer**
Irregular in the damaged area

- **Ca/Si ratio**
In the **intact** area, the CaCO_3
layer is only few μm thick
In **damaged** area, the formation
of CaCO_3 has reached deeper
regions of the material

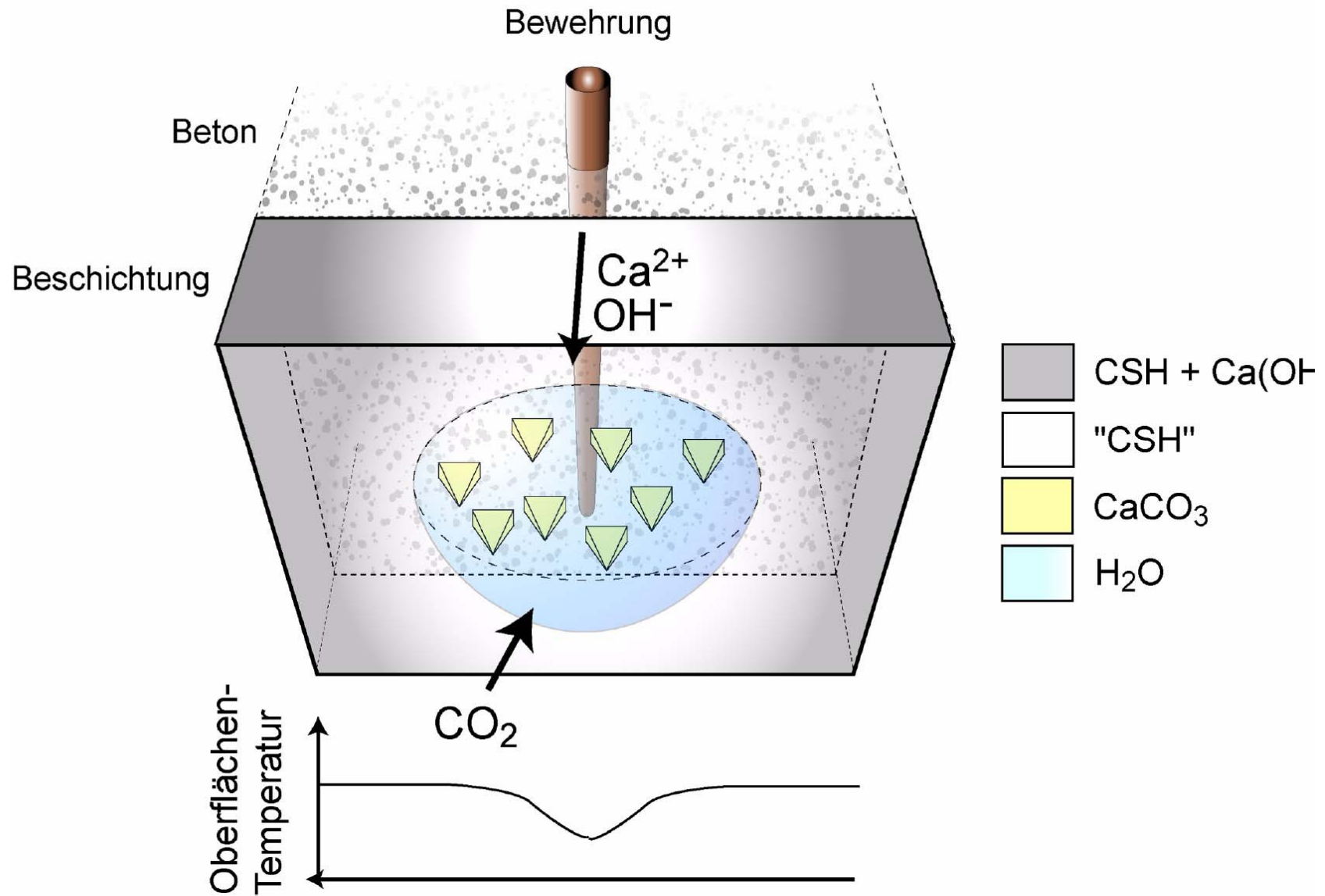


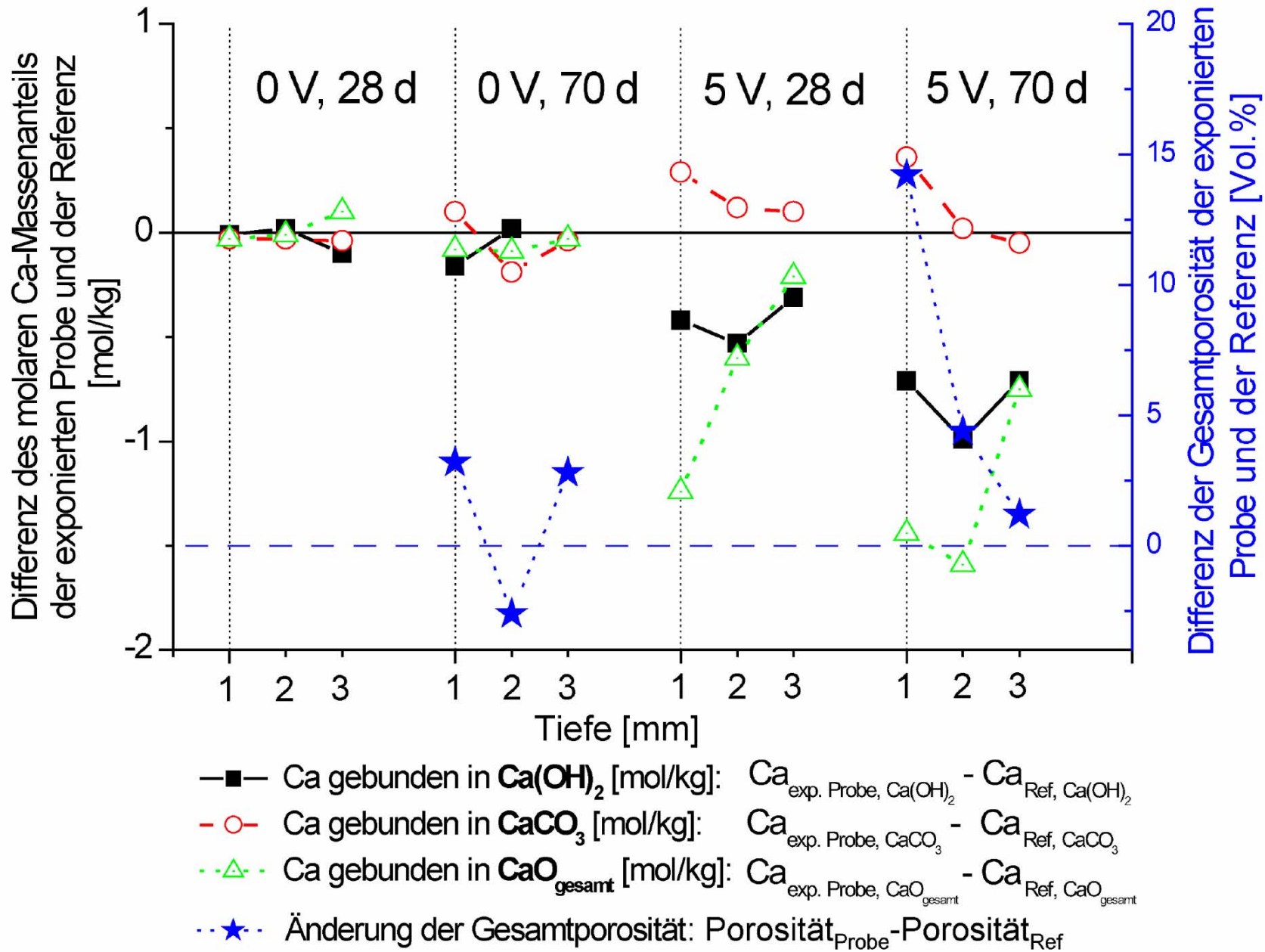
- The formation of a CaCO_3 -layer can play a...
 - **protective role** → fast crystallisation; Ca^{2+} and HCO_3^- from the water
 - **destructive role** → crystal growth affects the pore water chemistryIf Ca^{2+} is supplied by the pore solution, CaCO_3 formation triggers a further chemical degradation of the solid phases of the cement paste
- **Leaching** but also **CaCO_3 formation** causes microstructural changes in the CSH also by „decalcification shrinkage“
- An **initial leaching** can be crucial for the long-term behaviour of cement based materials in permanent contact with water (also if the water is considered to be „not aggressive“)
 - favorable conditions for CaCO_3 precipitation are shifted in deeper areas of the material
 - subsequent ingress of HCO_3^- and Ca^{2+} can occur only by diffusion
 - slow process – formation of a dense coating unlikely
- The structural properties of a CaCO_3 layer are determined by frame conditions (e.g. water composition, temperature) affecting the efficiency as a diffusion barrier

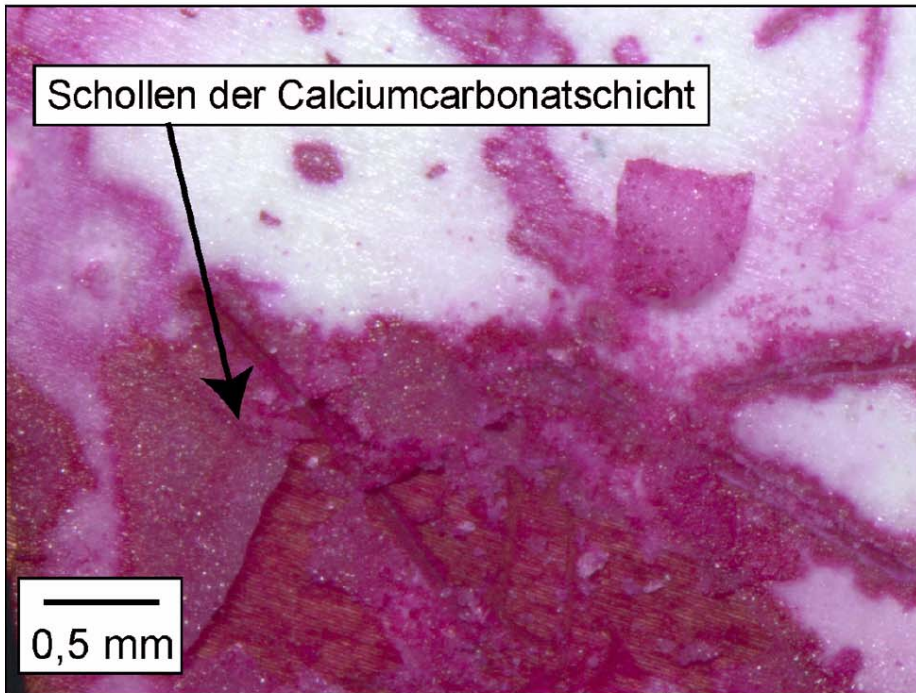
Thank you for your kind attention



← ~ 20 μm →







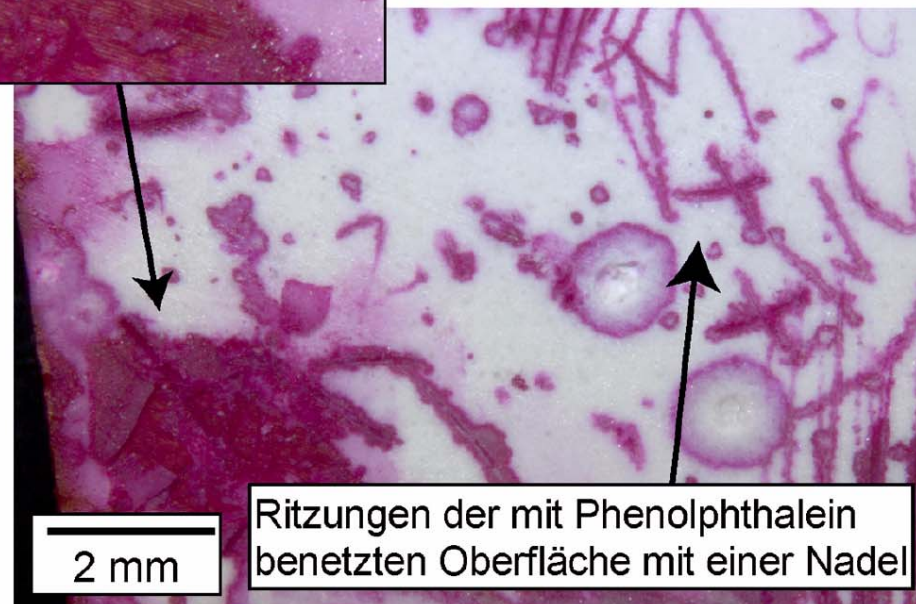
1. Phenolphthaleinlösung wurde auf die Oberfläche aufgebracht: Keine signifikante Farbreaktion

Calciumcarbonatschicht unterbindet den Kontakt der Indikatorlösung mit der alkalischen Porenlösung des Zementsteins.

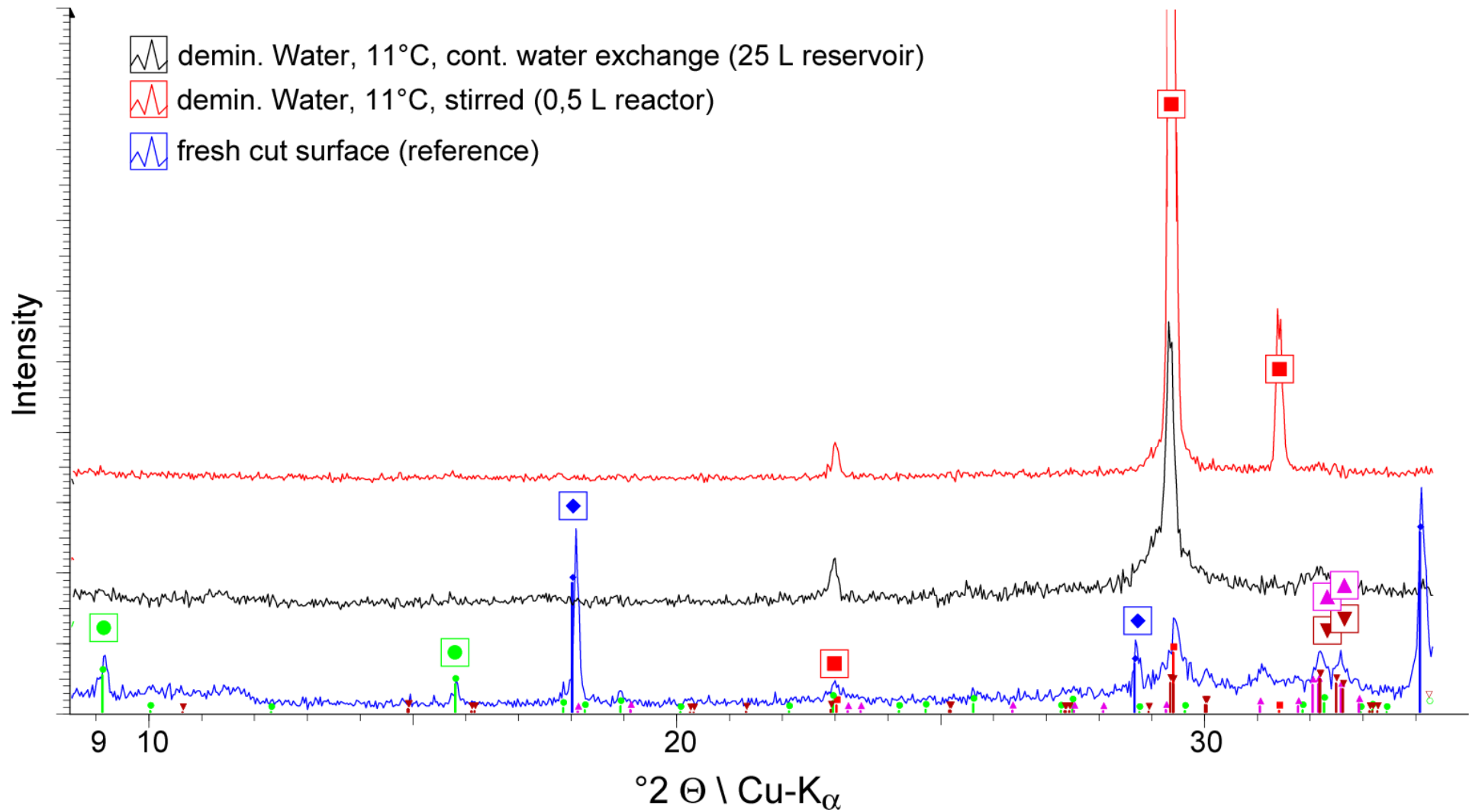
2. Anritzen der Oberfläche mit einer Nadel:




Im Bereich der Ritzung tritt violette Verfärbung auf






Nur in Bereichen, die mit einer Nadel angeritzt wurden, konnte die Indikatorlösung in Kontakt mit der alkalischen Porenlösung (pH ~12) des unter der Calciumcarbonatschicht liegenden Zementsteins kommen.



XRD of the sample surfaces



-  demin. Water, 11°C, cont. water exchange (25 L reservoir)
-  demin. Water, 11°C, stirred (0,5 L reactor)
-  fresh cut surface (reference)

-  05-0586 (*) - Calcite, syn - CaCO₃
-  44-1481 (*) - Portlandite, syn - Ca(OH)₂
-  41-1451 (*) - Ettringite, syn - Ca₆Al₂(SO₄)₃(OH)₁₂ · 26H₂O
-  33-0302 (*) - Larnite, syn - Ca₂SiO₄
-  86-0402 (C) - Hatrurite, syn - Ca₃SiO₅

Sättigungsindex Calcit (SI)

(bei pH 7.5, TA 3.5 mmol/L, Ionenstärke: 11 mmol/L, c(Ca): 2,5 mmol/L)

