



Gefördert durch:



Bundesministerium  
für Wirtschaft  
und Energie

aufgrund eines Beschlusses  
des Deutschen Bundestages

## Eva-M: Carbonate inhibitor applications in the Bavarian molasse basin

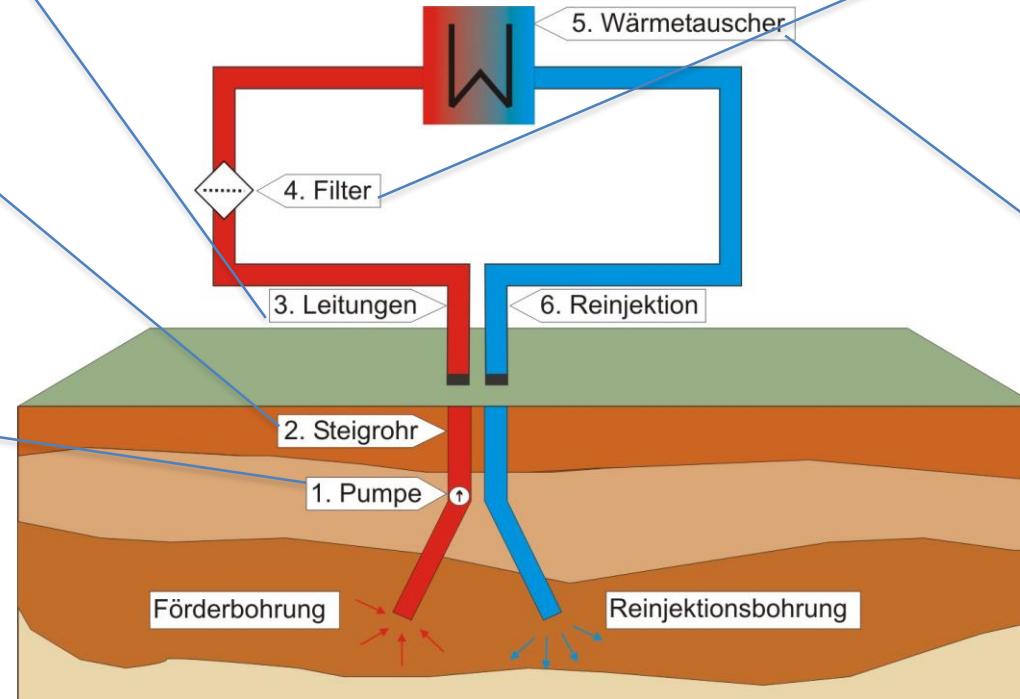
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# Carbonate scalings in the Bavarian Molasse Basin



→ Regular operation is not possible!



# Objectives of EvA-M

**EvA-M:** Einsatz von Ausfällungsinhibitoren im Molassebecken

Application of scaling inhibitors in hydrothermal projects of the Molasse Basin

**Goal of the project:** Multidisciplinary investigation, evaluation and interpretation of potential processes at the application of carbonate inhibitors

Laboratory experiments



On site experiments



Monitoring during operation

- Evaluation of performance and stability of inhibitor
- Evaluation of biological and chemical degradation of organic inhibitor
- Development of methods to detect the inhibitor
- Modelling of propagation of inhibitor in the reservoir



# Application of Inhibitors in hydrothermal plants in the Bavarian Molassebasin

Development and test of the inhibitor NC47.1B in the previous project „ThermoInhibitor“

Requirements on the inhibitor (governmental and operative):

- All applied substances have to be environmental friendly
- (water hazard class 1 or better)
- Biological and thermal degradable
- Longterm stability
- Good performance
- Economic application
- Longterm available



Source: Volkswagen AG



# Carbonate scalings in the Bavarian Molasse Basin

## Application of Inhibitors

### Definition Inhibitor

Inhibitors are substances, which are able to influence chemical, biological or physical reactions in a way that they become retarded, inhibited or avoided.



**Waschmaschinen leben  
länger mit Calgon.**





# Mode of operation of inhibitorw

## Complexation - Chelatation



## Threshold-effect

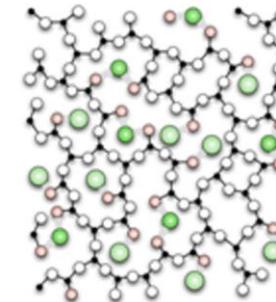
Supersaturated  $\text{CaCO}_3$ -solution

Precipitation of microcrystalline  $\text{CaCO}_3$   
(50 – 100 nm)

Crystals are bound by polyelectrolytes

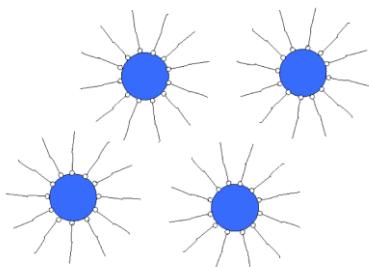
$\text{CaCO}_3$  concentration decreases below  
Saturation

No further precipitations

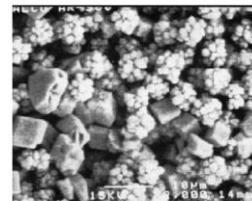
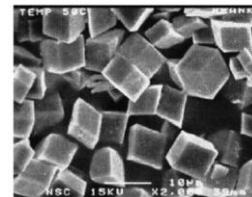


## Dispersion

Electrosteric stabilisation of  $\text{CaCO}_3$  crystals



Perturbation of crystal growth

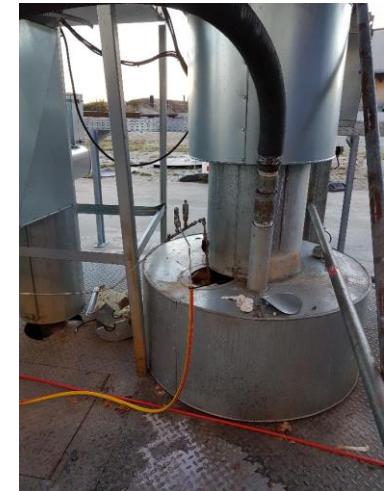


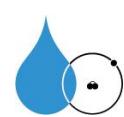
Source: Martin Sieben, Niederrheinchemie



# Application of the inhibitor NC47.1B in the geothermal plant Unterhaching

- Injection since August 2018
- In the first 5 days injection below pump, subsequently on the surface
- Hydrochemical, mineralogical and plant-specific monitoring  
(Production well, Injection well)





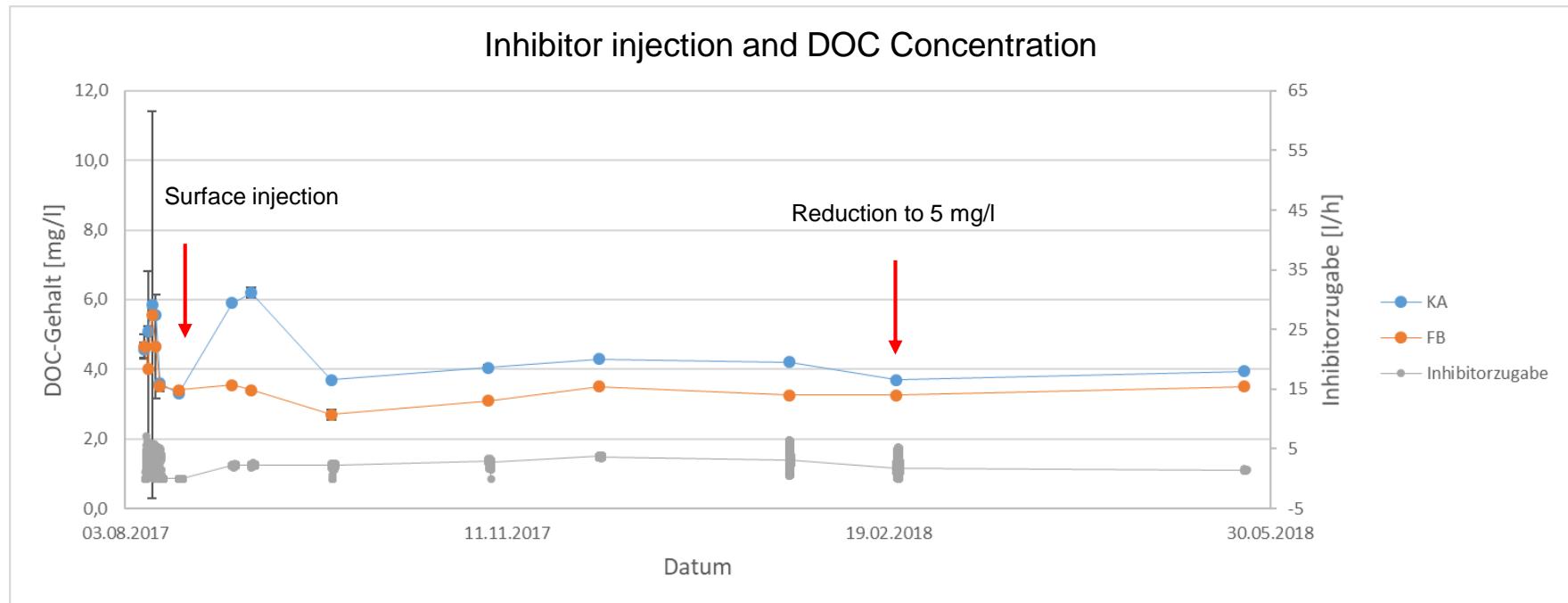
## Application of the inhibitor NC47.1B in the geothermal plant Unterhaching

- No carbonate precipitations on the filter and heat exchanger entrance
- ESP works since 14 months without problems
- Production of solids apparently decreased



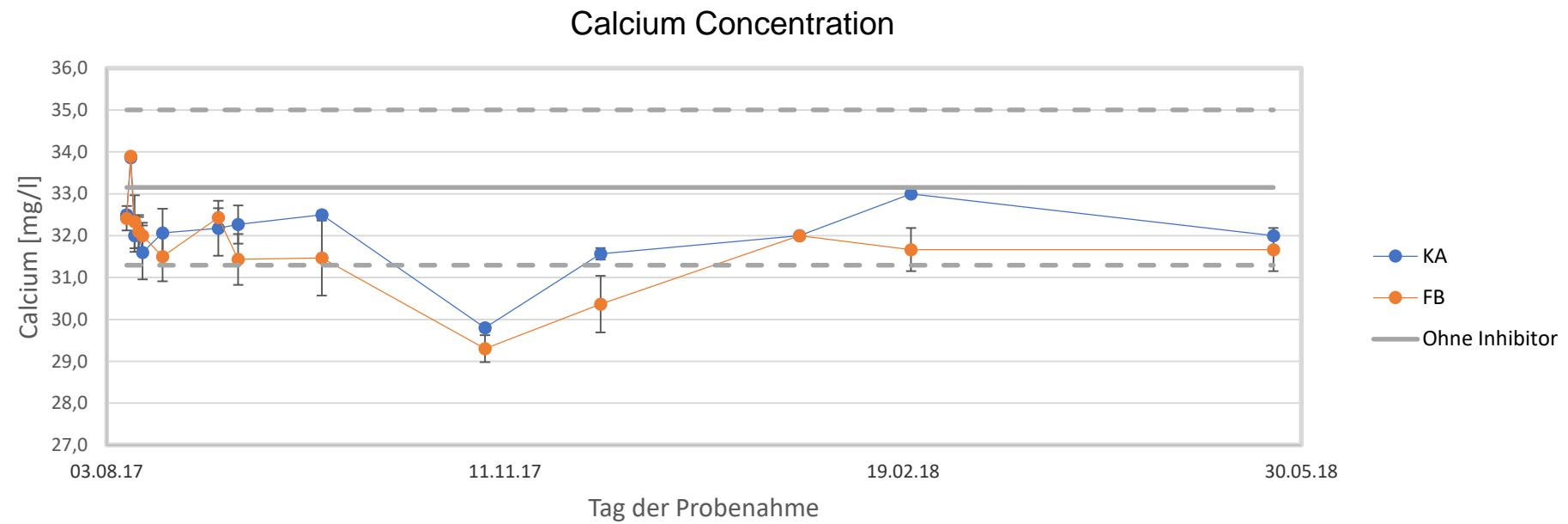


# Application of the inhibitor NC47.1B in the geothermal plant Unterhaching



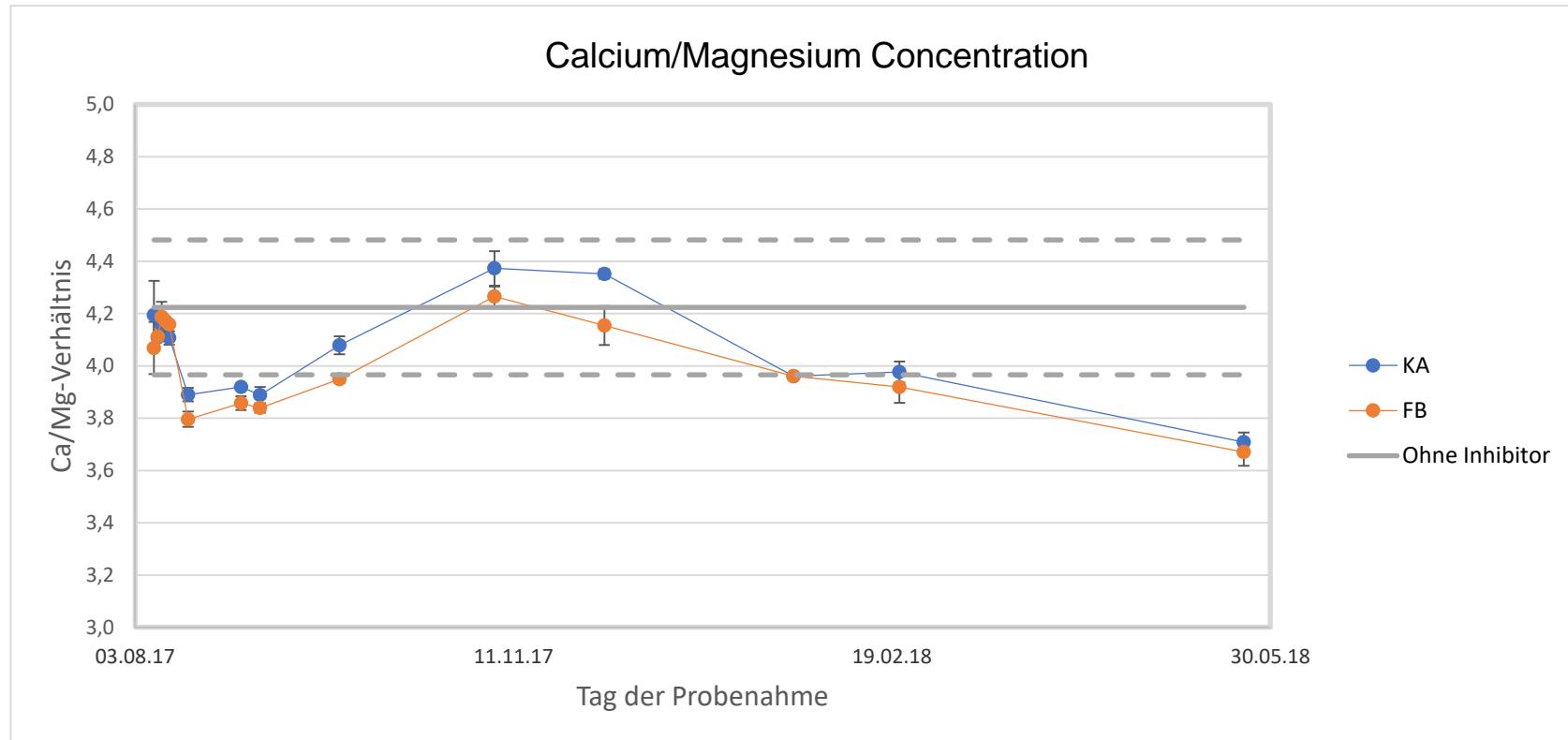


# Application of the inhibitor NC47.1B in the geothermal plant Unterhaching





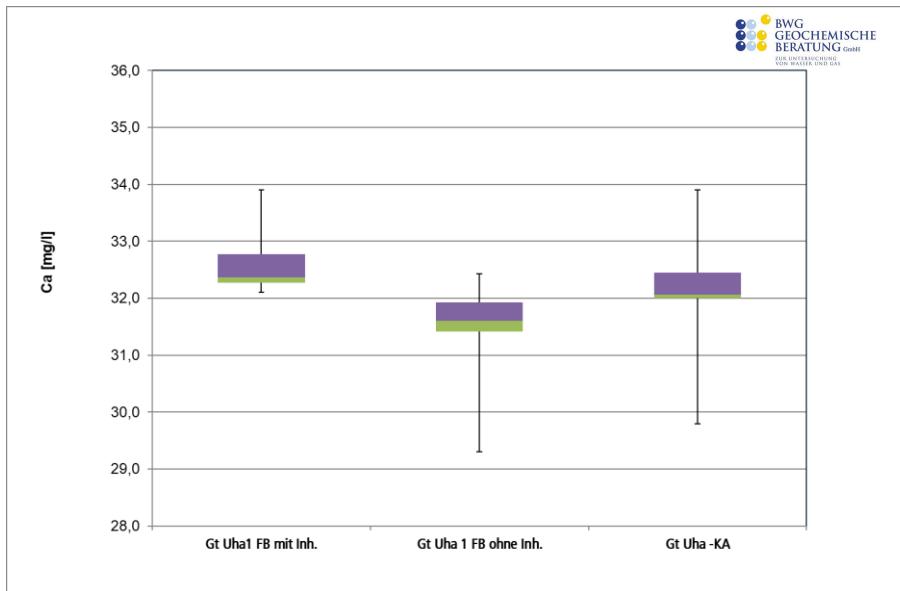
# Application of the inhibitor NC47.1B in the geothermal plant Unterhaching



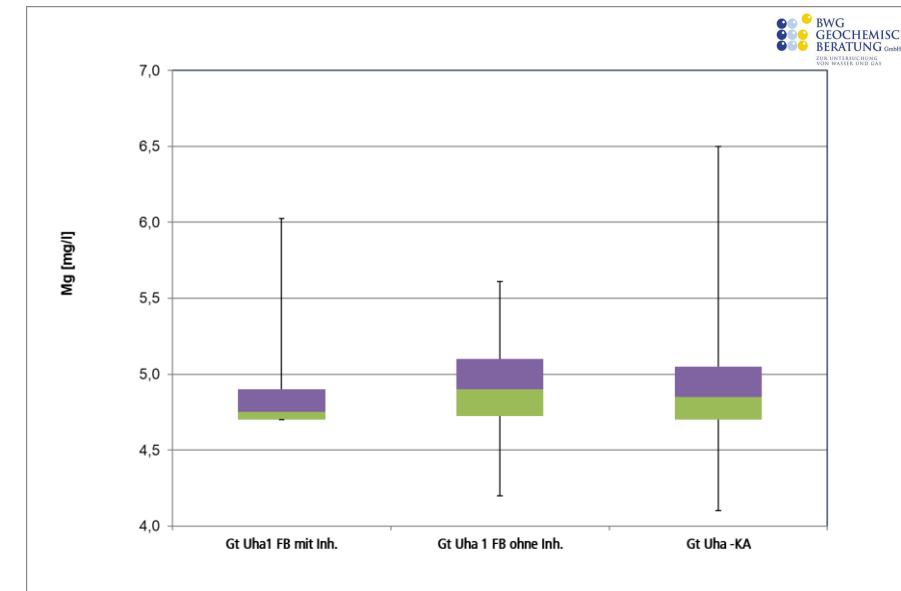


# Application of the inhibitor NC47.1B in the geothermal plant Unterhaching

## Dissolved Ca-concentration



## Dissolved Mg-concentration



Samples at production well with inhibitor:

4 (x3) samples

Samples at production well without inhibitor:

10 (x3) samples

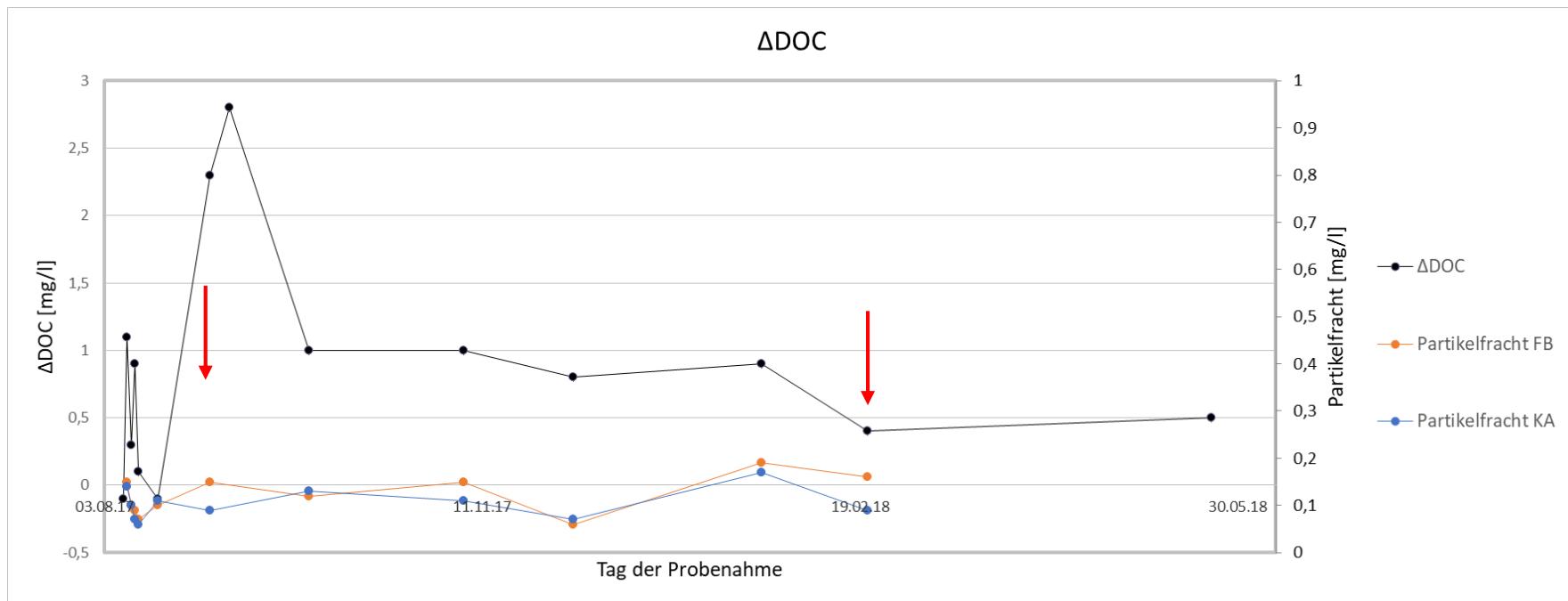
Samples before injection with inhibitor:

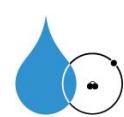
14 (x3) samples



# Application of the inhibitor NC47.1B in the geothermal plant Unterhaching

Particle concentrations at the production well (FB) and before injection (KA) as function of inhibitor concentration





# Application of the inhibitor NC47.1B in the geothermal plant Unterhaching

Probenahme	Particle Conc PW [mg/l]	Particle Conc In [mg/l]
08.08.2017	1.47	81.6
09.08.2017	0.15	0.14
10.08.2017	0.1	0.1
11.08.2017	0.09	0.07
12.08.2017	0.07	0.06
17.08.2017	0.1	0.11
31.08.2017	0.15	0.09
06.09.2017	n.b.	0.08
26.09.2017	0.12	0.13
06.11.2017	0.15	0.11
05.12.2017	0.06	0.07
24.01.2018	0.19	0.17 (0,16 Gt I2)
21.02.2018	0.16	0.09
06.08.2015	0.19	0.26 (Gt I2)

## Particle Concentrations

Amount of solids on 3 µm filters

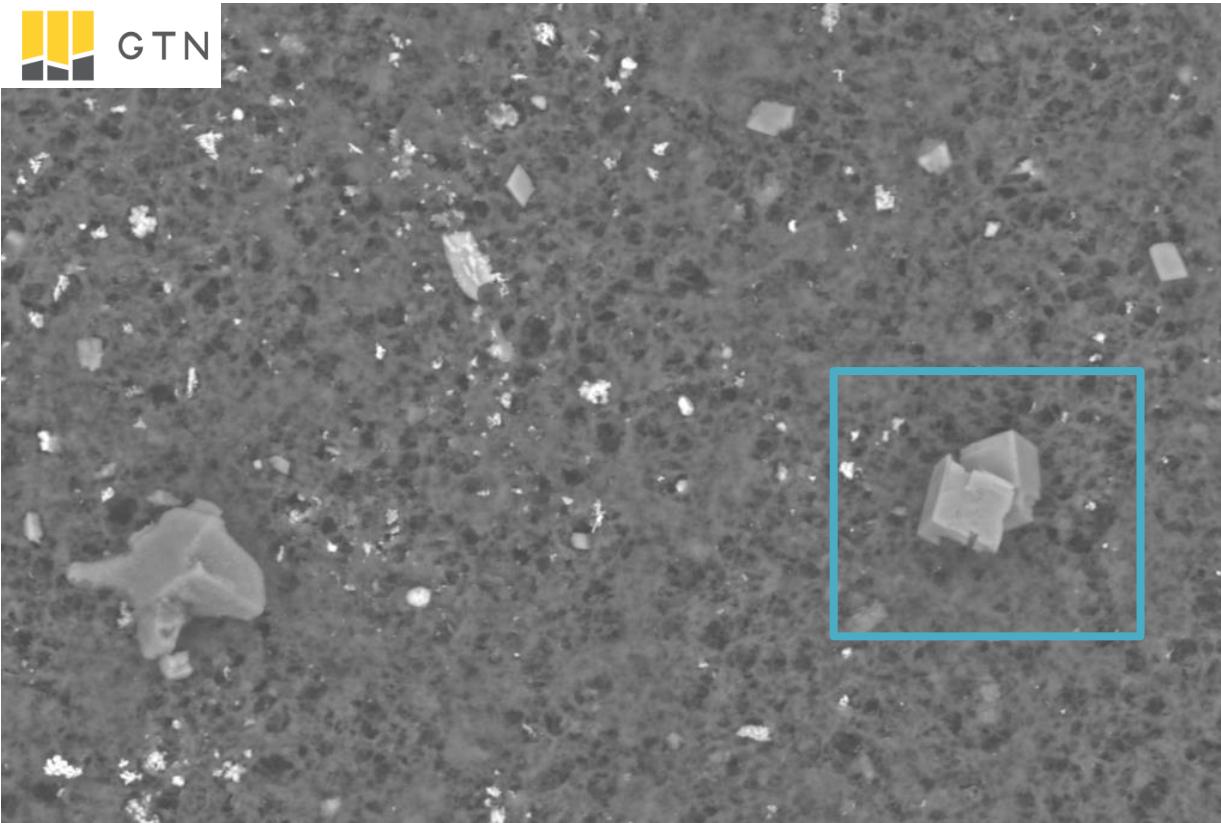
At beginning of operation high particle conc.  
due to cleaning residues at production well (PW)  
and before injection (In)

Following low particle concentrations on the  
production well and before injection

In comparison with 2015 reduced particle conc.  
due to application of inhibitor



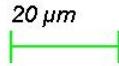
# Application of the inhibitor NC47.1B in the geothermal plant Unterhaching



Production well

05.12.17

Idiomorphic Calcite



20  $\mu\text{m}$

EHT = 20.00 kV  
WD = 8.5 mm

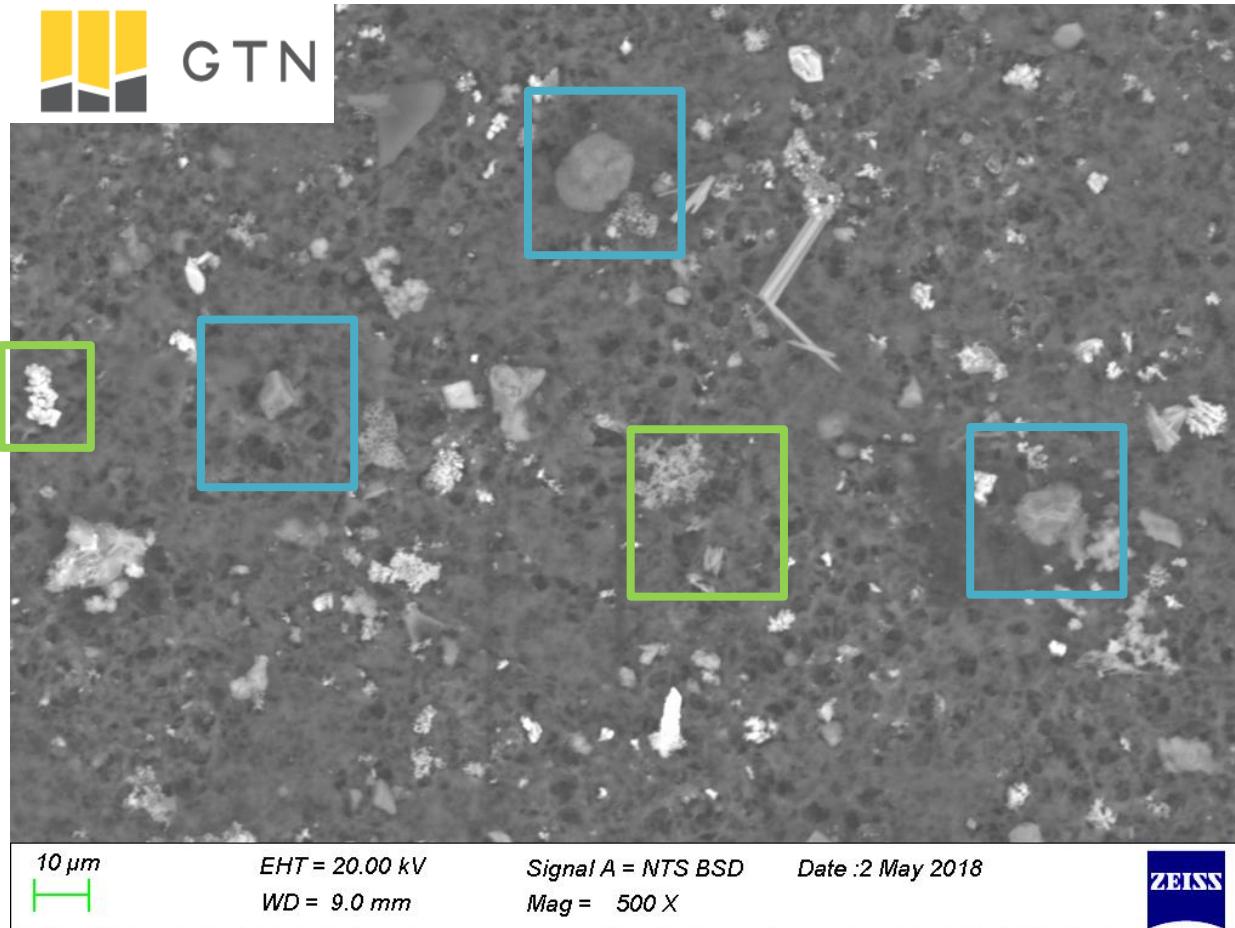
Signal A = NTS BSD  
Mag = 500 X

Date : 2 May 2018





# Application of the inhibitor NC47.1B in the geothermal plant Unterhaching



**Before Injection**

05.12.17

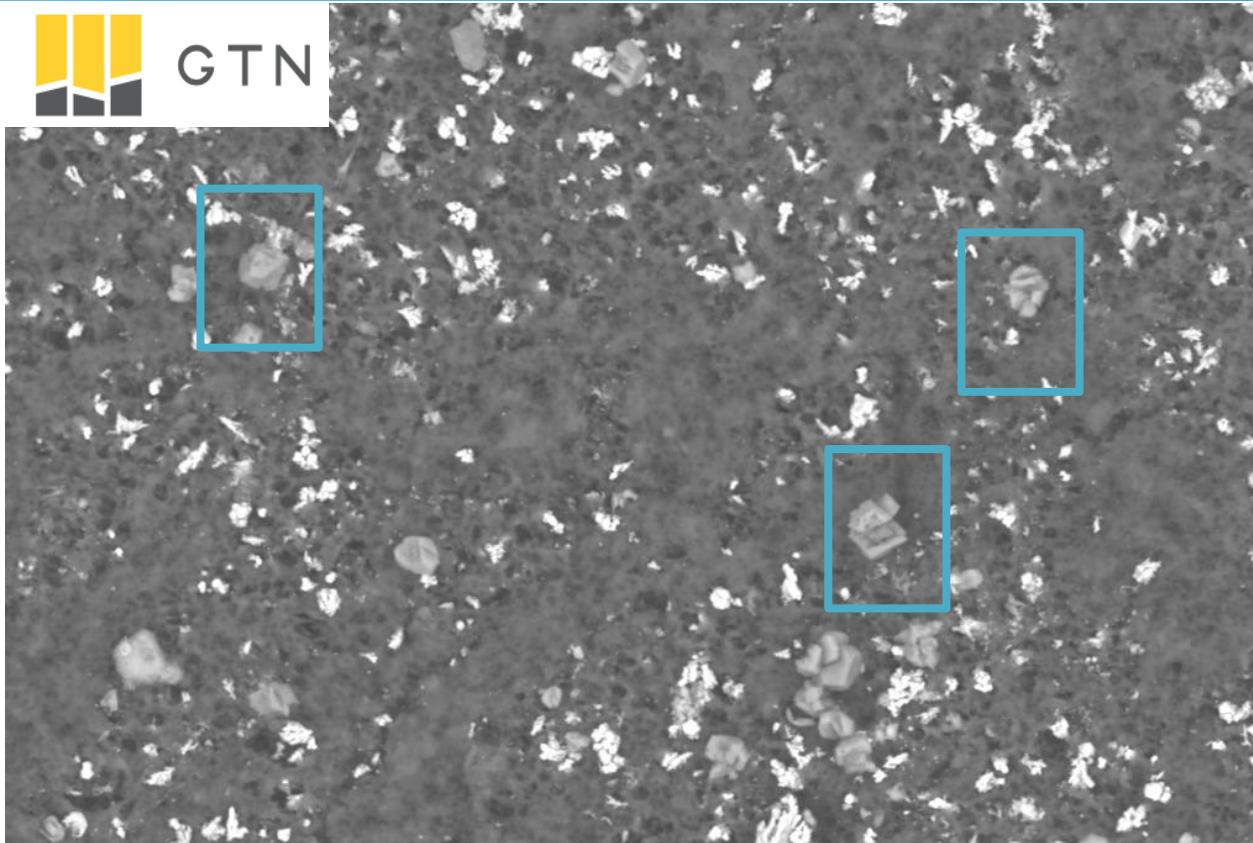
Xenomorphic calcite (blue)

Sulfides (green)





# Application of the inhibitor NC47.1B in the geothermal plant Unterhaching



10  $\mu\text{m}$   
H

EHT = 20.00 kV  
WD = 8.5 mm

Signal A = NTS BSD  
Mag = 500 X  
Date : 2 May 2018



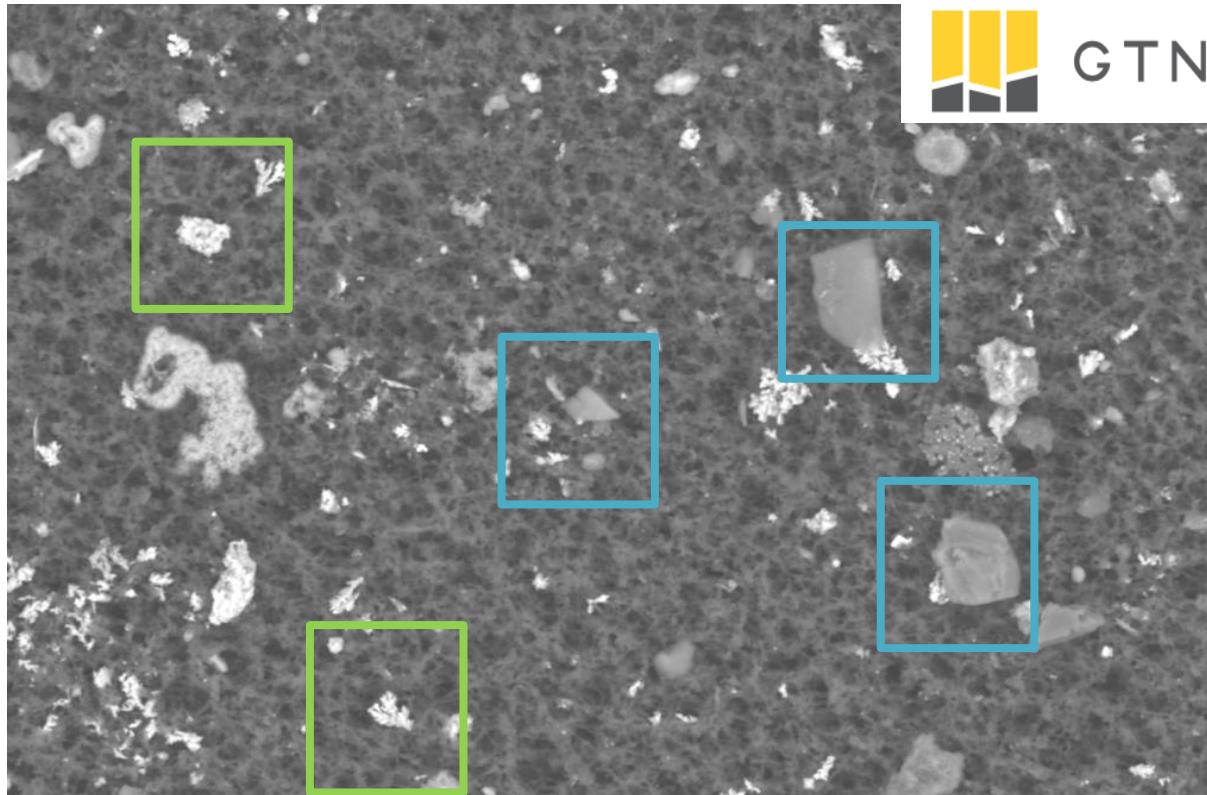
## Production well

21.02.18

Idiomorphic calcite



# Application of the inhibitor NC47.1B in the geothermal plant Unterhaching



G T N

Before Injection

21.02.18

Hypidiomorphic calcite(blue)

Sulfides (green)



Inhibitor concentration  
apparently to low



10  $\mu\text{m}$

EHT = 20.00 kV  
WD = 8.5 mm

Signal A = NTS BSD  
Mag = 500 X  
Date : 2 May 2018

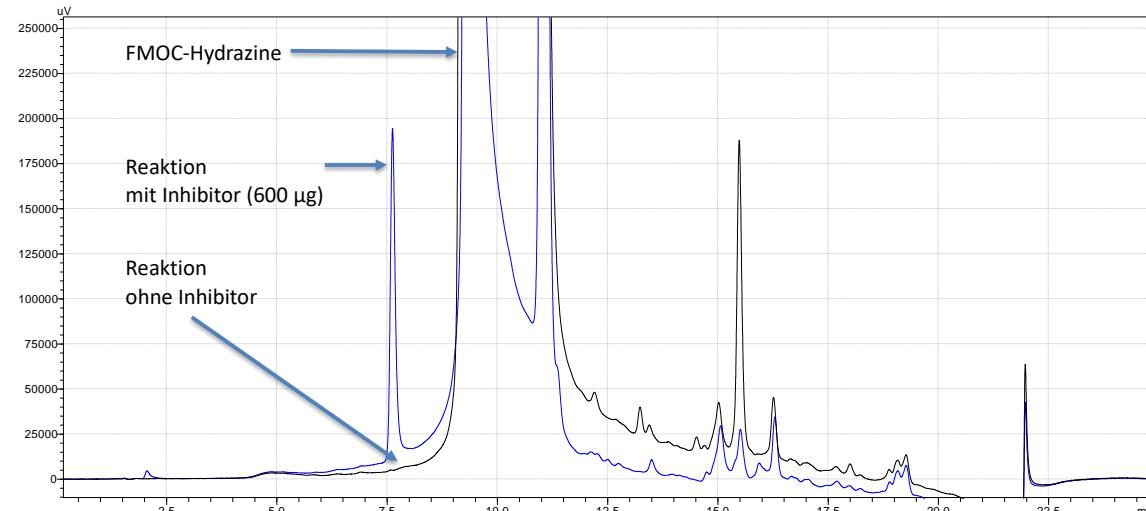




# Evaluation of scaling inhibitors for the Bavarian Molasse Basin

## Development of detection methods

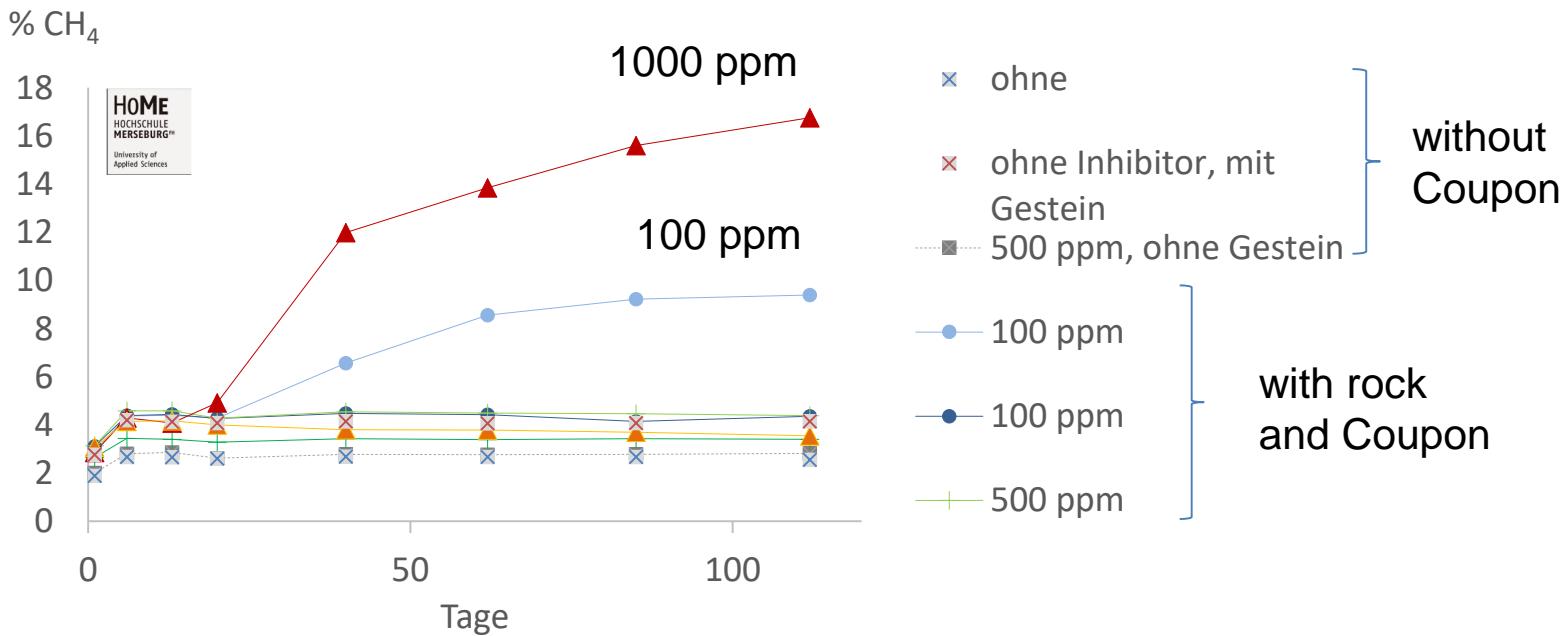
- Inhibitor can be detected by photometric and chromatographic (HPLC) methods and isotope analyses ( $^{14}\text{C}$ -DOC)
- Detection limit: app. 0.1 mg/l → Goal 0.01 mg/l





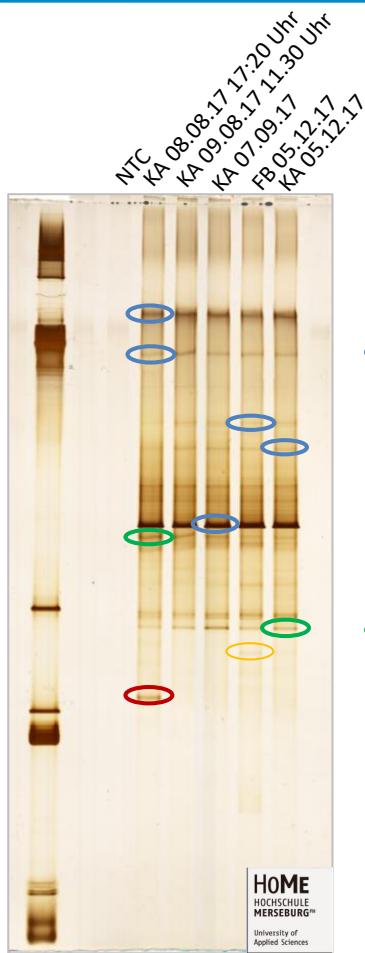
# Evaluation of scaling inhibitors for the Bavarian Molasse Basin

## Evaluation of microbial degradation of inhibitor





# Composition of microbial biocenosis



Sequential analysis ( BlastN-software)

95%-99% Similarity

○ Ralstonia sp.

○ Desulfotomaculum sp. → Sulfate reducer

○ Thermoanaerobacter sp.

○ uncultured bacterium



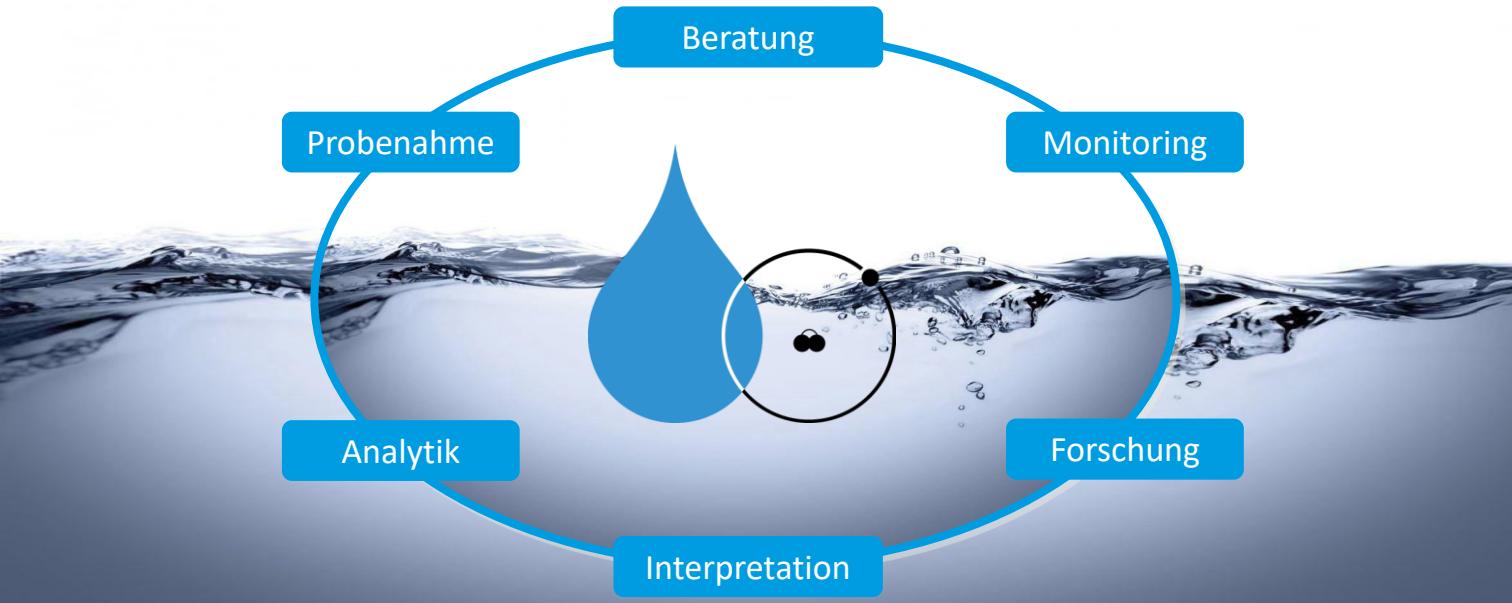
## Summary

- Inhibitor NC47.1B shows a good performance in operation
- Inhibitor concentration could be reduced during plant application
- Labexperiments confirm the long-term stability
- Labexperiments show that inhibitor is biodegradable
- Inhibitor can be detected



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