TECHNISCHE UNIVERSITÄT
BERGAKADEMIE FREIBERG
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Bundesministerium für Wirtschaft und Energie

Gefördert durch das Bundesministerium für Wirtschaft und Energie
Koordiniert durch den Projektträger Jülich

# Preventing calcite scales in deep geothermal wells and plants

# Modeling aspects

Broder Merkel & Alireza Arab

# Solubility of calcite

$CaCO_{3(s)} \rightarrow Ca^{2+} + CO_3^{2-}$ T↑

$CO_{2(g)} \rightarrow CO_{2(aq)}$ T↓ P ↑

$CO_{2(aq)} \rightarrow HCO_3^- + H^+$

$H^+ + CO_3^{2-} \rightarrow HCO_3^-$

$Ca^{2+} + CO_3^{2-} + H^+ = CaHCO_3^+$

$Ca^{2+} + SO_4^{2-} = CaSO_4^0$

$Ca^{2+} + PO_4^{3-} = CaPO_4^-$

$Ca^{2+} + CH_2O^{2-} = CaCH_2O$

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1) depending on temperature

2) extremely fast

Saturation index (SI)

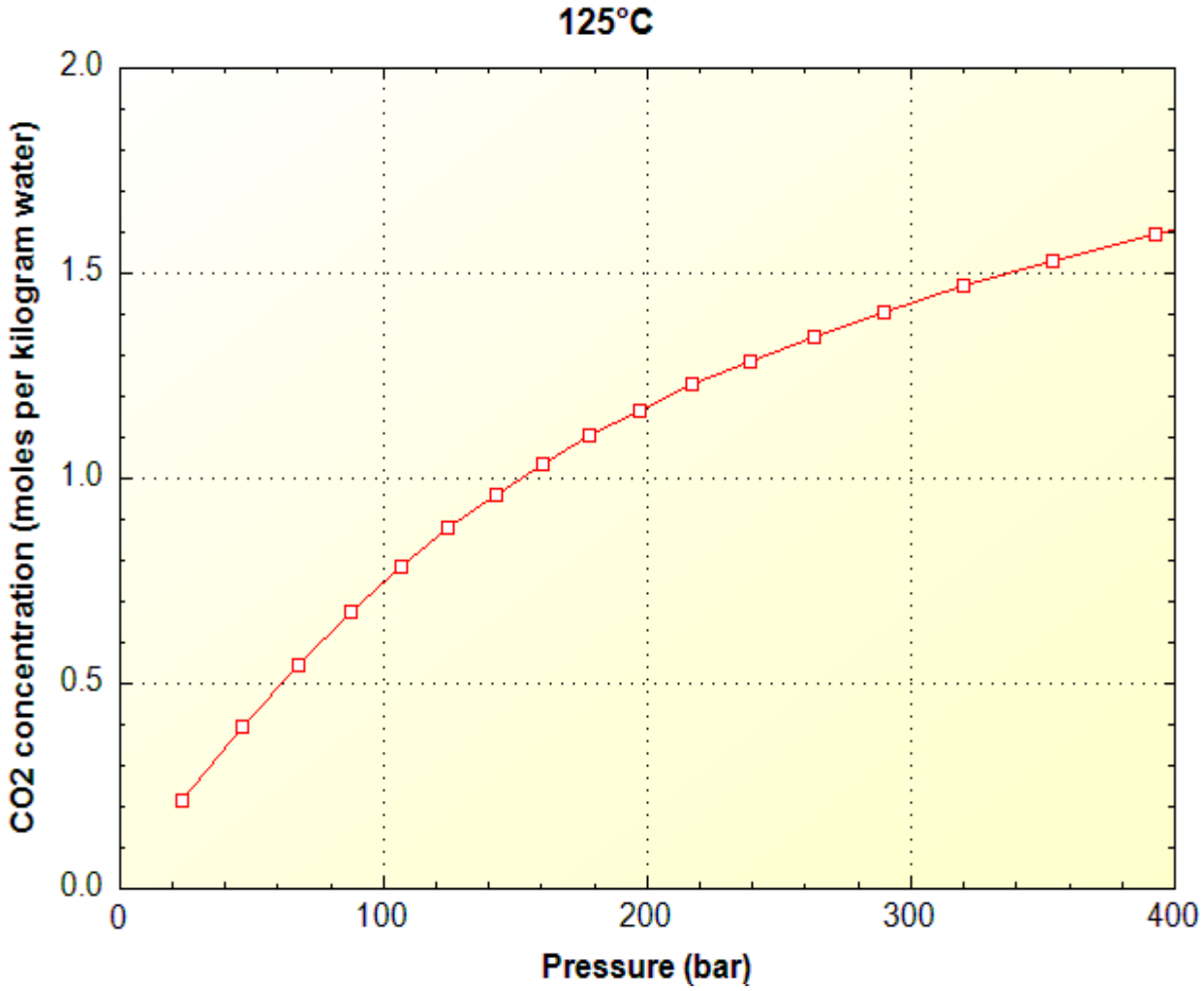
$$SI = \log\left(\frac{IAP}{K}\right)$$

# Gas solubility

1 to 50 bar: Henry's law

> 50 bar Peng-Robinson EOS

$C_{gas} = K_H \cdot p_{(gas)}$



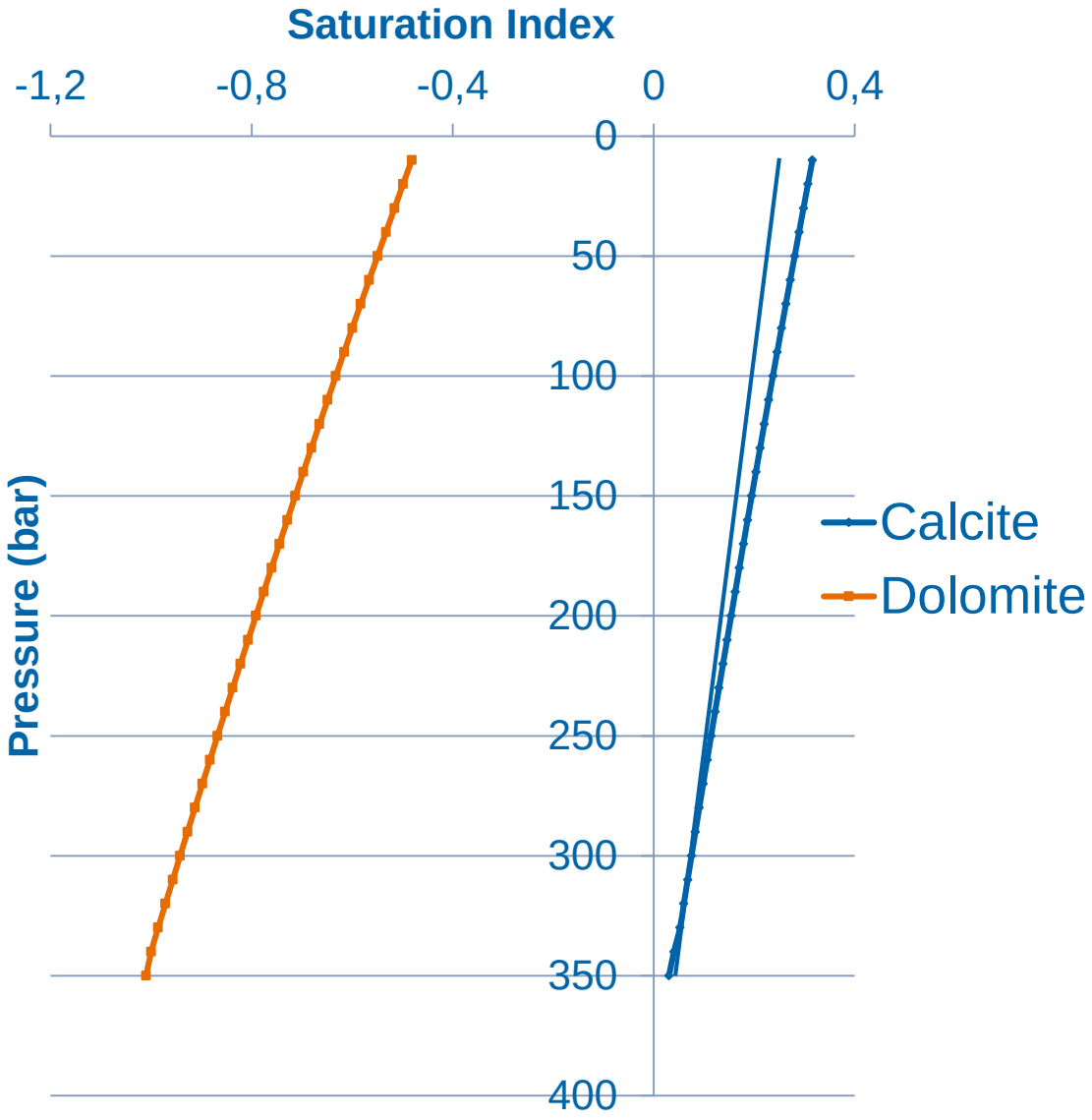

Peng-Robinson EOS

$$p = \frac{RT}{V_m - b} - \frac{a\alpha}{V_m^2 + 2bV_m - b^2}$$

$$a = \frac{0{,}457235 \cdot R^2 T_c^2}{p_c}$$

$$b = \frac{0{,}077796 \cdot RT_c}{p_c}$$

# Problem of deep geothermal production well in a carbonate aquifer (steady state: 125°C)




But:

- Precipitation occurs
- Precipitation is kinetically controlled

# Kinetics of calcite dissolution and precipitation

## Plummer & Busenberg

$$R = F^k \cdot (k1 \cdot aH^+ + k2 \cdot aCO_2 + k3 \cdot aH_2O)(1 - 10^{(\frac{2}{3} \cdot SI)})$$

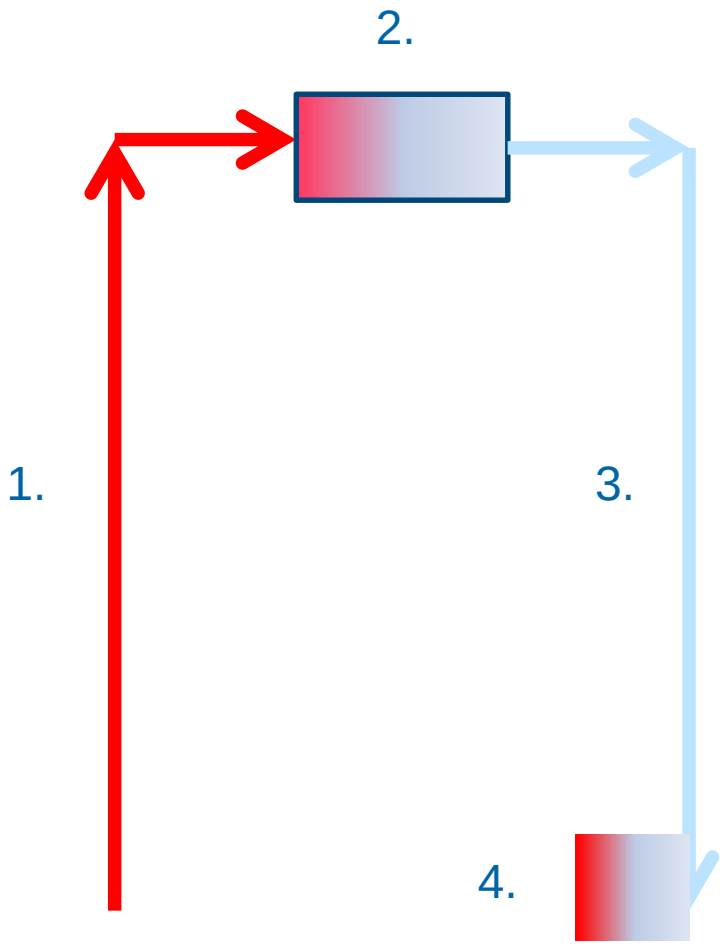
R= rate (mol/s)
F= area ($cm^3$ per mol calcite); k = exponent
k1, k2, k3 = thermodynamic constant ; a = activity of species

## But:

- Dissolution and precipiation may be different
- $CO_2$ diffusion $\leftrightarrow$ water
- Laminar or turbulent flow
- Inhibitors

→ Additional terms

# Problems in deep geothermal carbonate dominated systems under steady state conditions




1. Pressure decrease
   → scaling in riser pipe and pump

2. Temperature decrease
   → scaling in heat exchanger

3. Pressure increase

4. Temperature increase

# How can the scaling problem be solved?

Keep SI < 0

$CaCO_{3(s)} \rightarrow Ca^{2+} + CO_3^{2-}$

$CO_{2(g)} \rightarrow CO_{2(aq)}$

$CO_{2(aq)} \rightarrow HCO_3^- + H^+$

$H^+ + CO_3^{2-} \rightarrow HCO_3^-$

$Ca^{2+} + CO_3^{2-} + H^+ = CaHCO_3^+$

$Ca^{2+} + SO_4^{2-} = CaSO_4^0$

$Ca^{2+} + PO_4^{3-} = CaPO_4^-$

$Ca^{2+} + CH_2O^{2-} = CaCH_2O$

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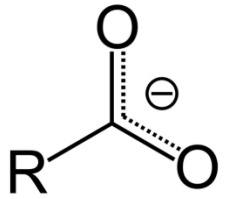
# EvA-M research project funded by BMWI *)
# Utilization of degradable inhibitor
# Modeling part

ROI: Molasse basin, south of Munich

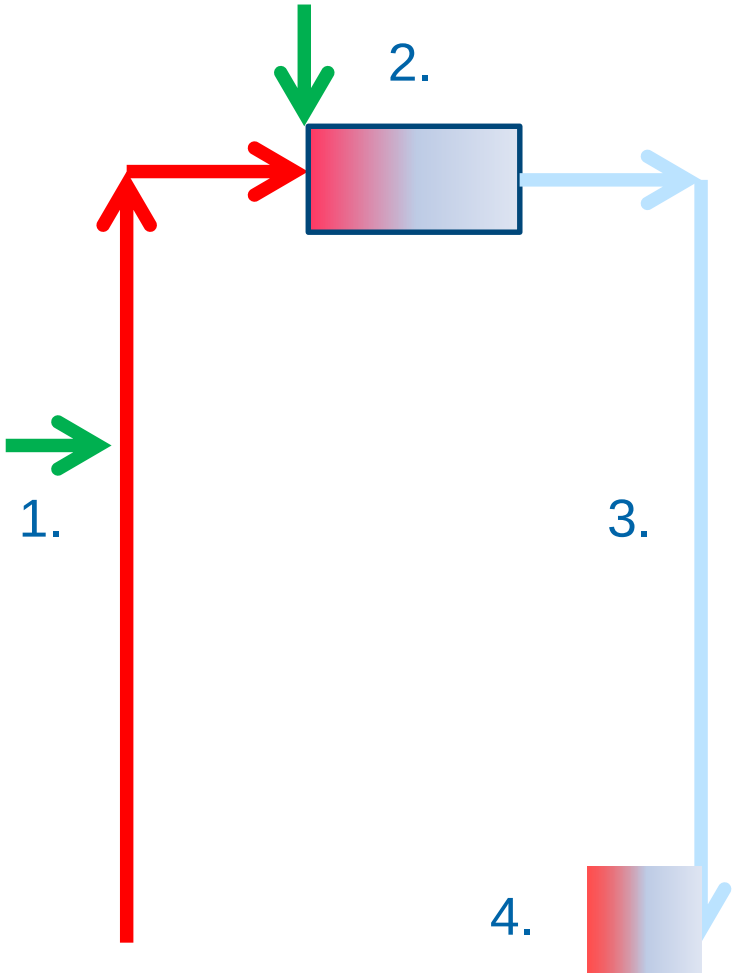
NC47.1B : mixture of bio-degradable polycarboxylates with carboxyl groups




- Inhibits the growth of calcite crystals
- Forms complexes with $Ca^{2+}$ and other cations
- Experiments to determine log-K values (surface-complexation, complexation)

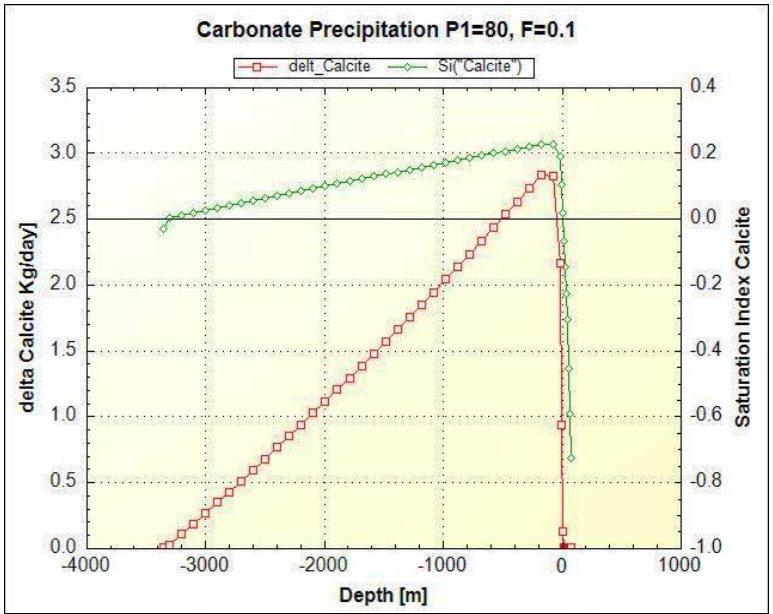
*) BMWI: Federal Ministry for Economic Affairs and Energy

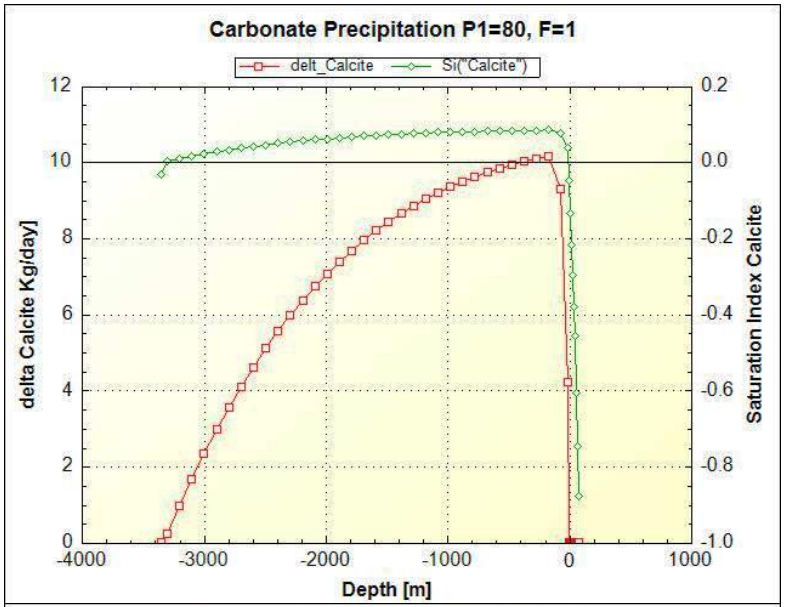
# Reactive transport model

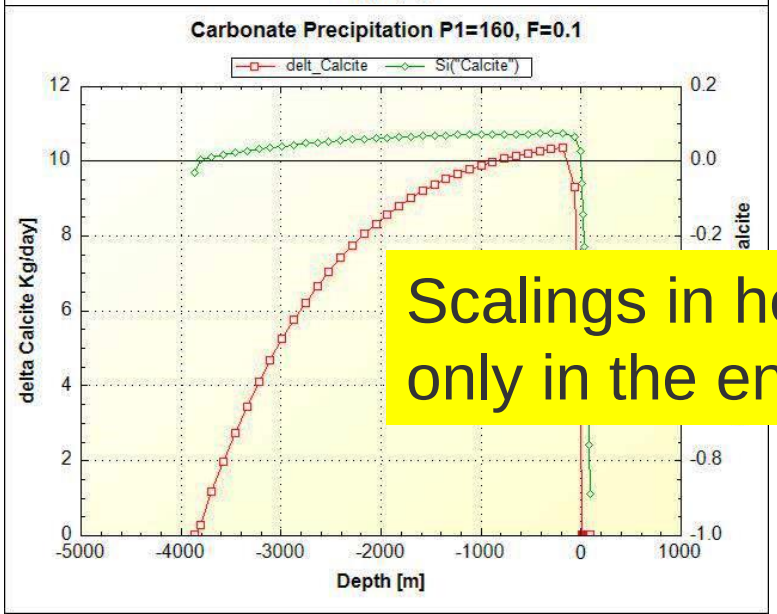


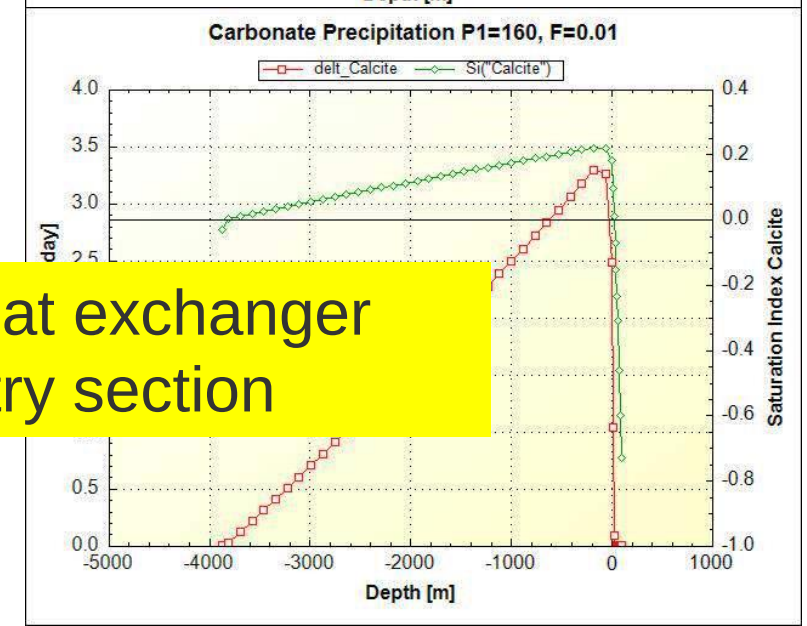

- Injection points
- Mixed log-K approach
- Degradation of NC47.1B depending on temperature and time
- Bio-film?

# Reactive transport model (prod. well / heat exchanger) delta calcite and SI for different kinetics parameters



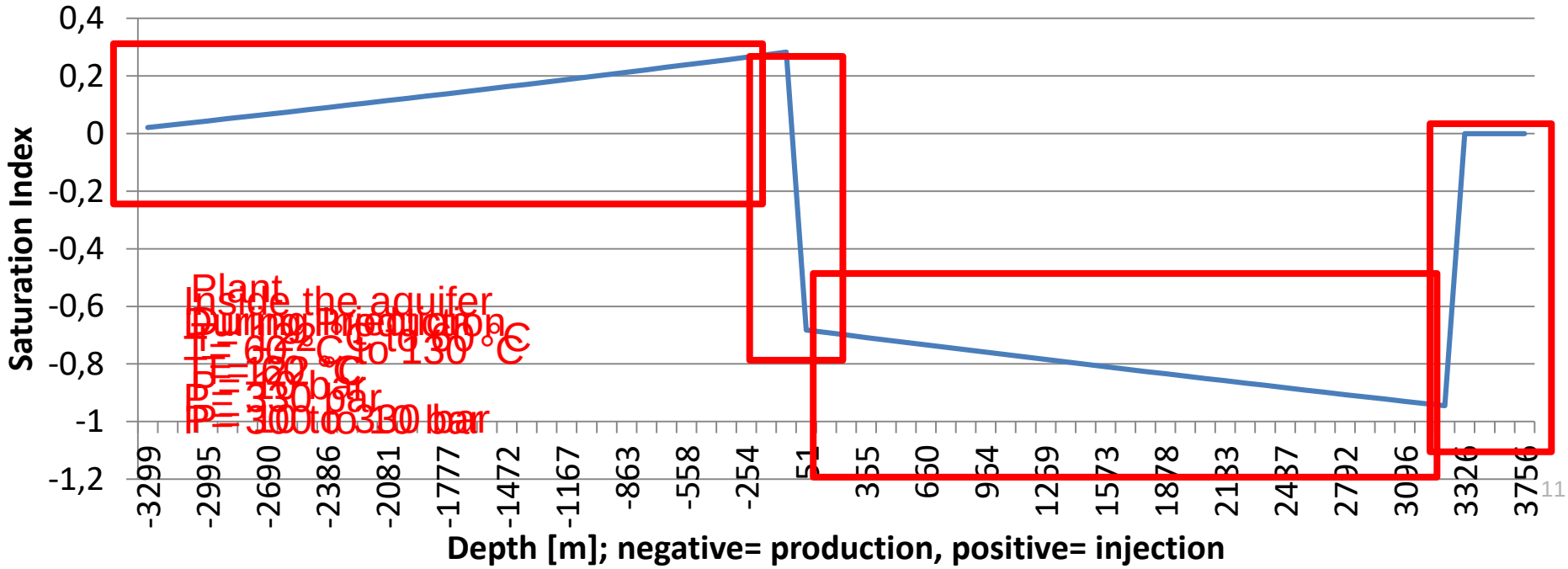




Scalings in heat exchanger only in the entry section

# Reactive transport model

PHREEQC Version 3; phreeqc.dat (Peng Robinson EOS)

- Chemical composition, pH, redox-couples and Eh
- Pressure and temperature
- Thermodynamics
- Kinetics of calcite precipitation and dissolution



# Conclusion and outlook

1D kinetic PHREEQC model with Peng-Robinson EOS including production well, heat exchanger, injection well and near field aquifer

Log-K values for inhibitor: subject of ongoing investigations

Spread of cold water in injection well will be replaced by 3D TOUGHREACT model

This includes dissolution of calcite and improving permeability of aquifer

Decomposition of inhibitor