Lessons learned from long-term corrosion investigations and –monitoring in saline thermal waters

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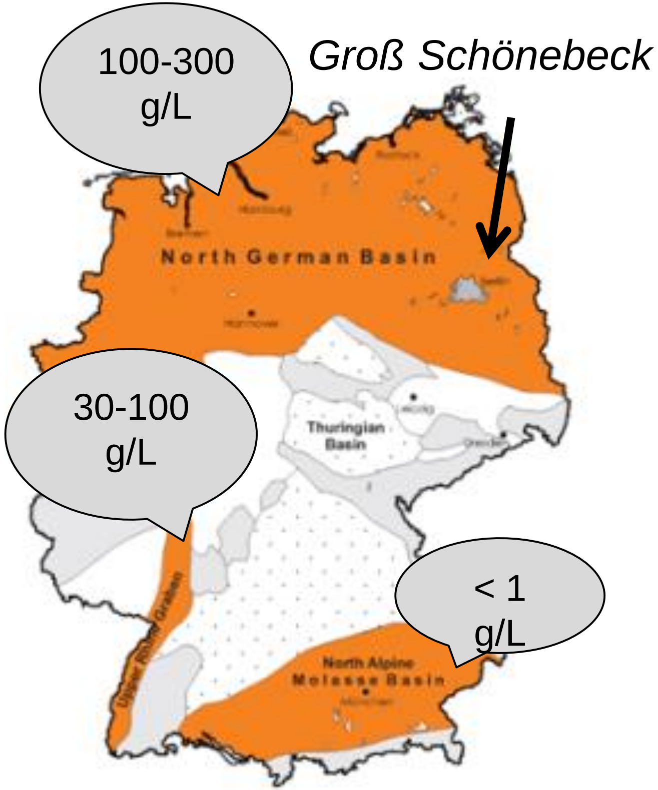
Corrosion in saline waters

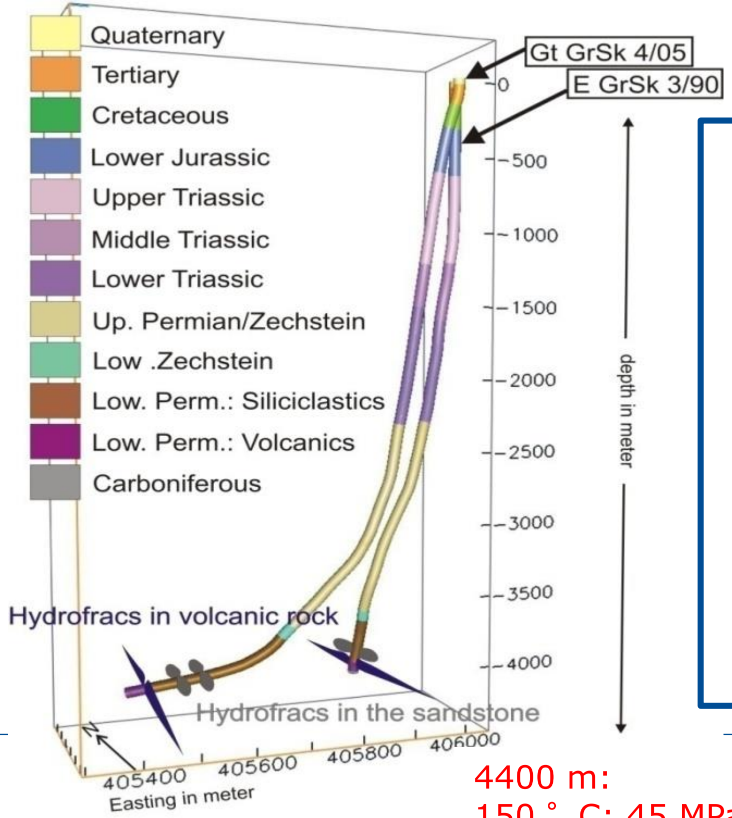
Geothermal fluids are corrosive.

High salinity increases corrosion of steel components.

Considerations on material selection before setting up a geothermal well and installations



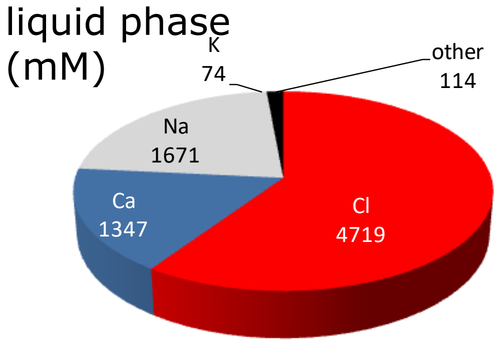
Background: The geothermal research platform Groß Schönebeck

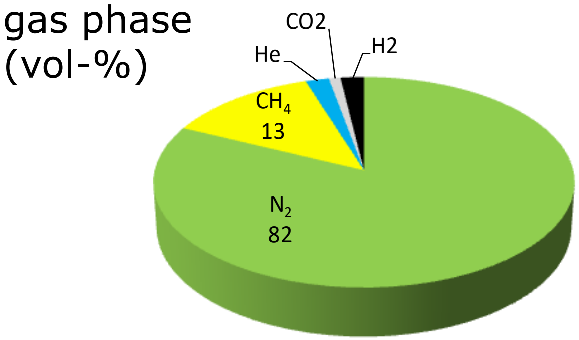


4400 m:
150 ° C; 45 MPa

fluid composition: 265g/L

liquid:gas ~1:1





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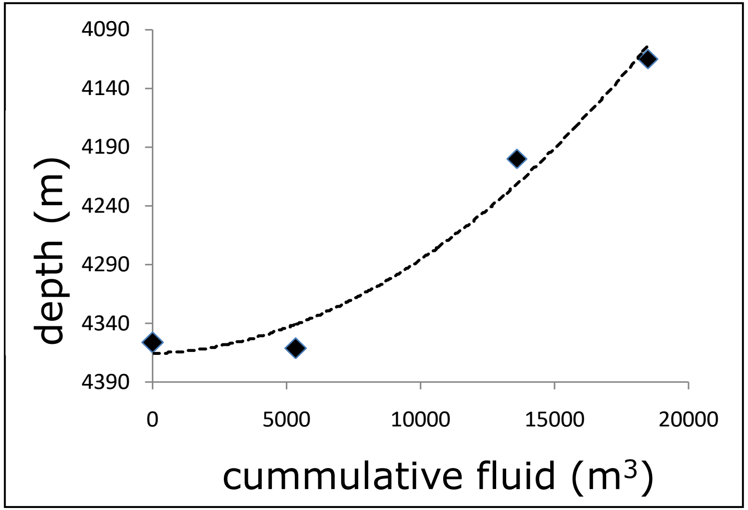
Groß Schönebeck circulation tests (2011-2013)



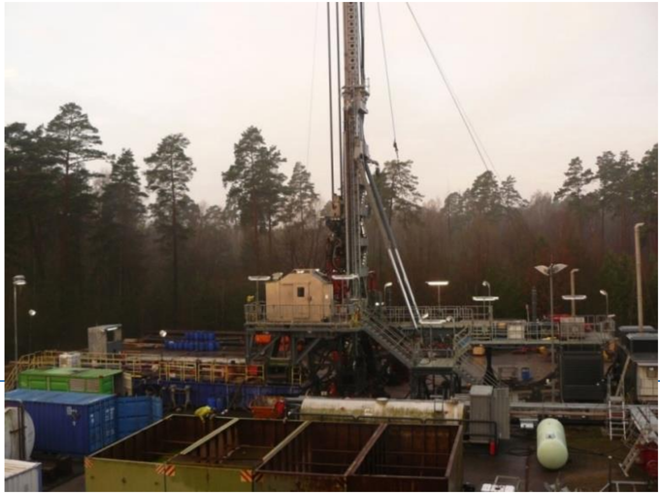
1. Reduced production rate and change of total depth over time.

2. Bailer sampling

indicated: filling of the production well (native copper, magnetite, barite…)

3. Removal of the fill:

1. Coiled tubing
2. Work-over rig



Blöcher et al., 2015; Reinsch et al., 2015; Regenspurg et al., 2015

Chemical monitoring – during and after circulation tests

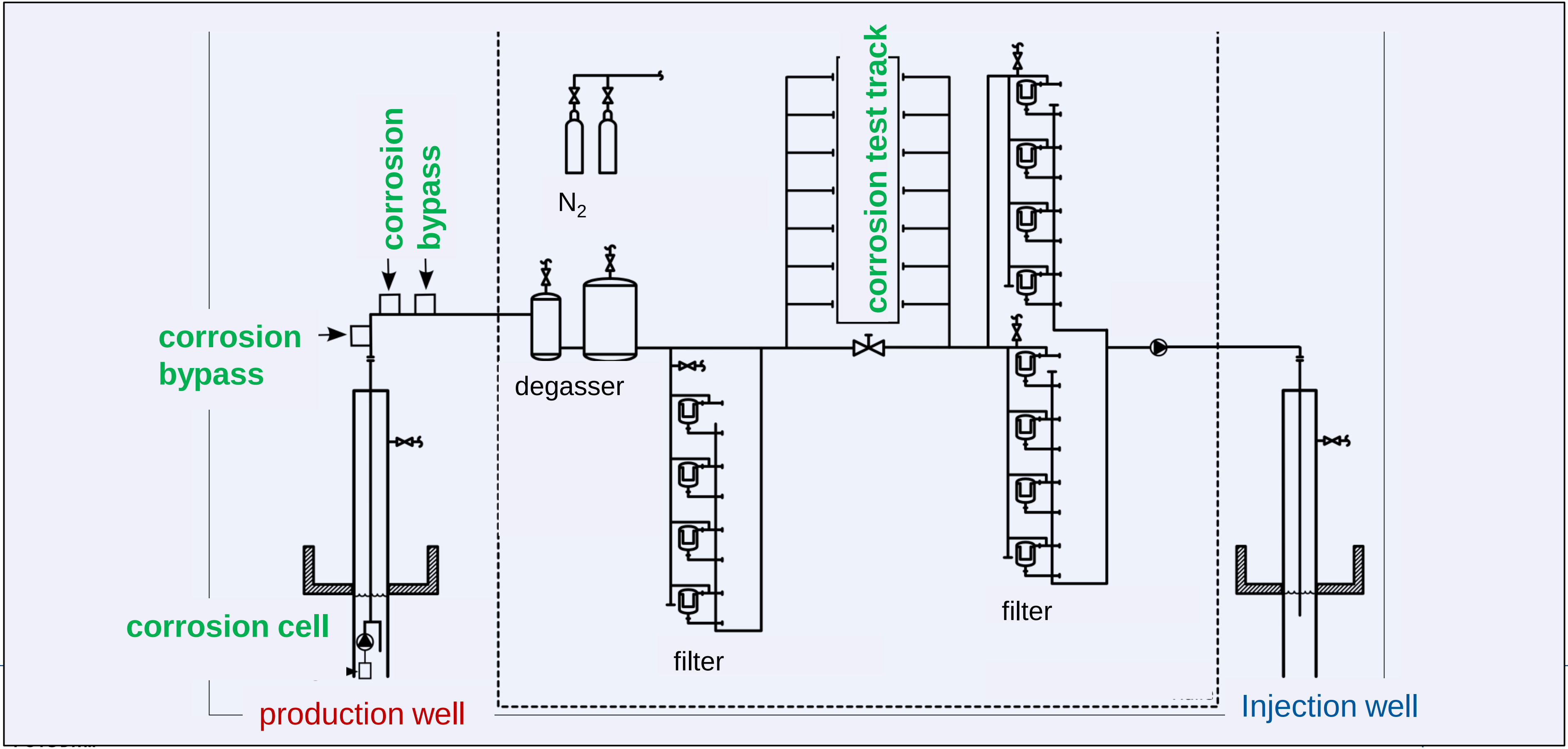
- Thermal water composition
  Feldbusch et al., 2013; Regenspurg et al. 2016
- Gas composition
  Feldbusch et al., 2018
- Solid phase composition
  Regenspurg et al., 2015
- **Corrosion**




Material protection: epoxy resin (Vetco TK236)

- Non-polar, electric isolating coating
- Temperature restistivity: 200 ° C
- thickness: < 250 µm

Corrosion monitoring



Corrosion monitoring

1. Corrosion test track (bypass)
2. Component bypass
3. Corrosion cell (below production pump)

} planned

4. Coating instability (tubing)
5. Wellbore: electrochemical corrosion

} unexpected

1. Monitoring corrosion test track

S+C materials (cast and modeling treatment)

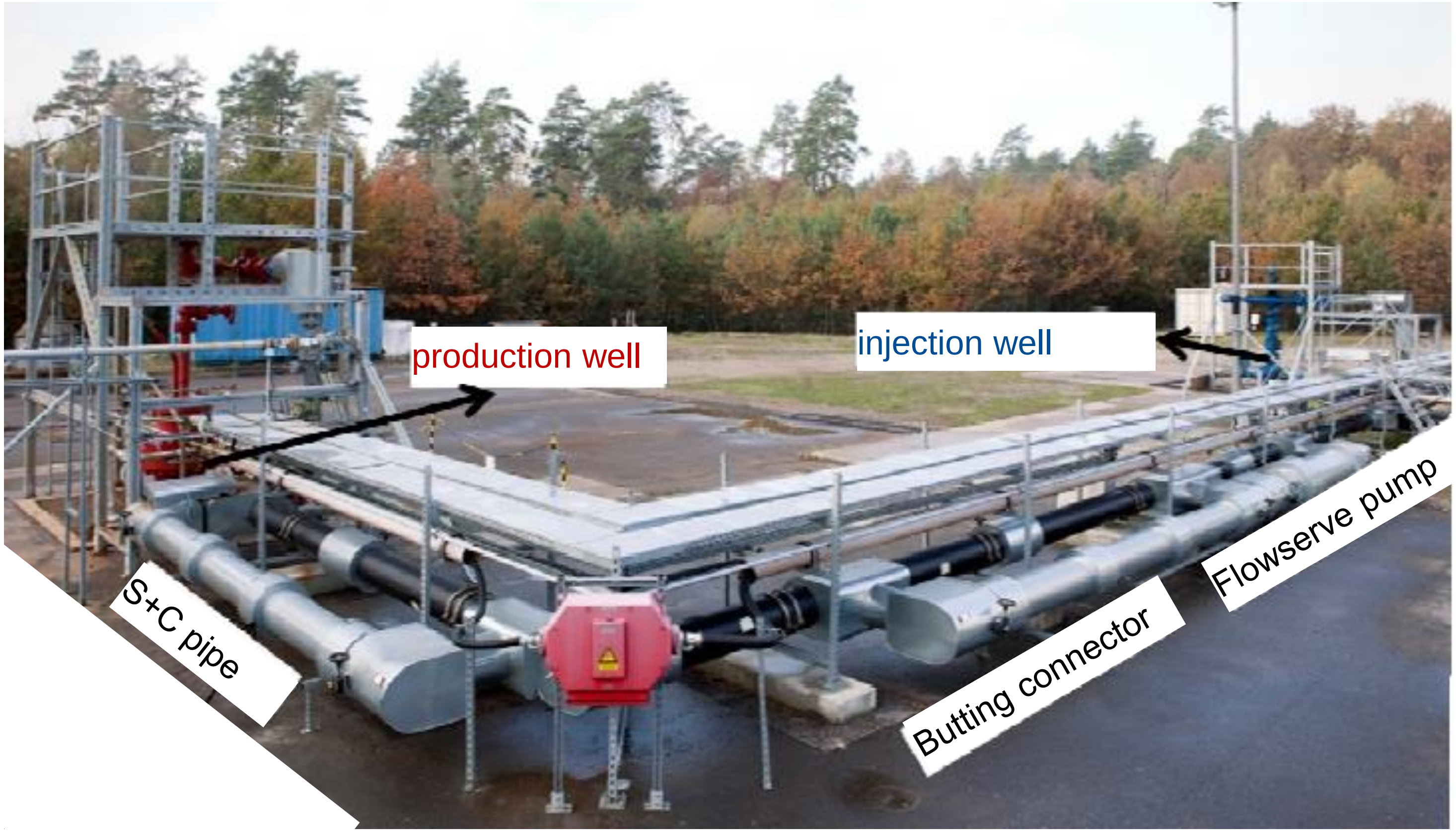
alloy	corrosion
G 45 Mo	no pitting corrosion
G 45 Mo mod.	
A59	
A 254 SMO	matted but no pitting
A625	
A825	
A31	
G625	
316 L	pitting corrosion
C80L	general corrosion

corrosion resistant

limited stable

unstable

2. Components (bypass)



2. Results components (bypass)

alloy	corrosion
Duplex cast material 1.4469	No corrosion
Superduplex 1.4501	
Austenitic cast steel 1.4408	
CrNiMo steel 1.4418	
Carbon steel parts	general corrosion (< 0.2 mm/a)

vane housing

corrosion resistant

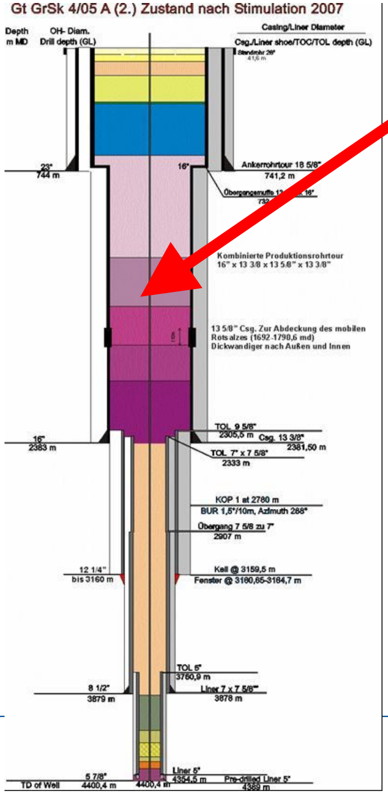
Little corrosion

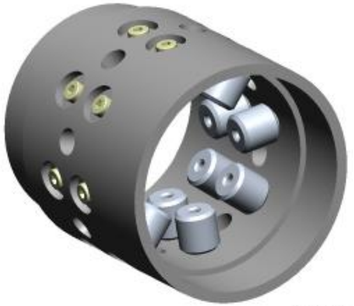
3. Corrosion test cell below the production pump

Production well

ESP in 1200 m

Corrosion test cell





Test cell

3. Results: corrosion-tests below the pump

- austenitic CrNiMo-steel A
- austenitic CrNiMo- Stahl B
- titanium gr. 12
- alloy 625
- alloy 59
- alloy 31
- alloy G45 Mo (7%)
- alloy G45 Mo (9,5%)

Example sample after 3 years exposure

→ all samples were corrosion-resistant
→ possibly corrosion protection by scaling

Unexpected corrosion reactions

4. Coating instability: Epoxy resin (Vetco TK236)

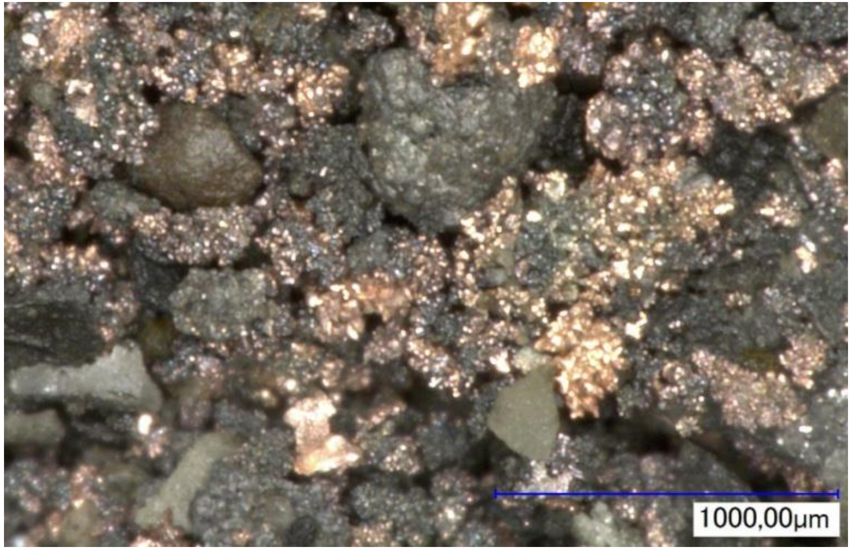
Tubing above ground: scaling *(barite)*, intact coating; adherence > 20,68 Mpa

Tubing (<1200m) below ground:

some tubes: coating removal

→ decreasing adhesion between topcoat and primer (red) → defect of manufacturing

5. Electrochemical corrosion in the well bore/ liner wall



Corrosion products: High amounts of

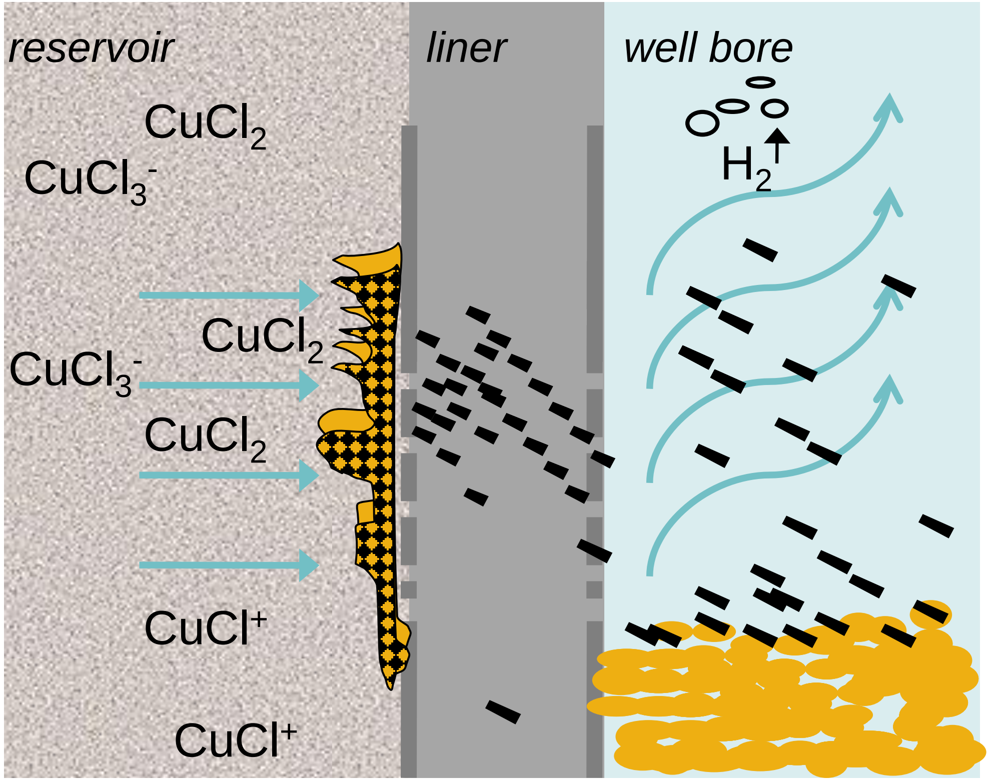
- native copper (Cu)
- magnetite (Fe_3O_4)

found at well bottom

- hydrogen gas (H_2)

masured in the gas phase

5. Electrochemical corrosion in the well bore



Corrosion process:

$Cu^{2+} + 2e^- \rightarrow Cu_0$ $\quad E_0 = 0.34\ V$

$Fe_0 \rightarrow Fe^{2+} + 2e^-$ $\quad E_0 = -0.44\ V$

$Fe_0 + 2H_2O \rightarrow Fe(OH)_2 + H_2$

$3Fe(OH)_2 \rightarrow Fe_3O_4 + H_2O + 2H_2$

$Cu^{2+} + 3Fe_0 + 4H_2O \rightarrow Cu + Fe_3O_4 + 8H_2$

Summary monitoring

- Most tested materials (apart of carbon steel) proved to be corrosion resistant within the installations.
- Stability of coatings cannot be guaranteed.
- Main risk: Electrochemical corrosion of carbon steel casing with dissolved Cu.

Corrosion prevention strategy

Use of higher alloyed casing:

- corrosion resistant (T, salinity, Cu^{2+})
- available for casing
- economically feasible

Cladded tubes

→ Combining properties of C-steel (stability and ductility) with corrosion resistivity of highly alloyed steels

→ Cladding of C-steel inside and/or outside by mechanical or metallurgical technique

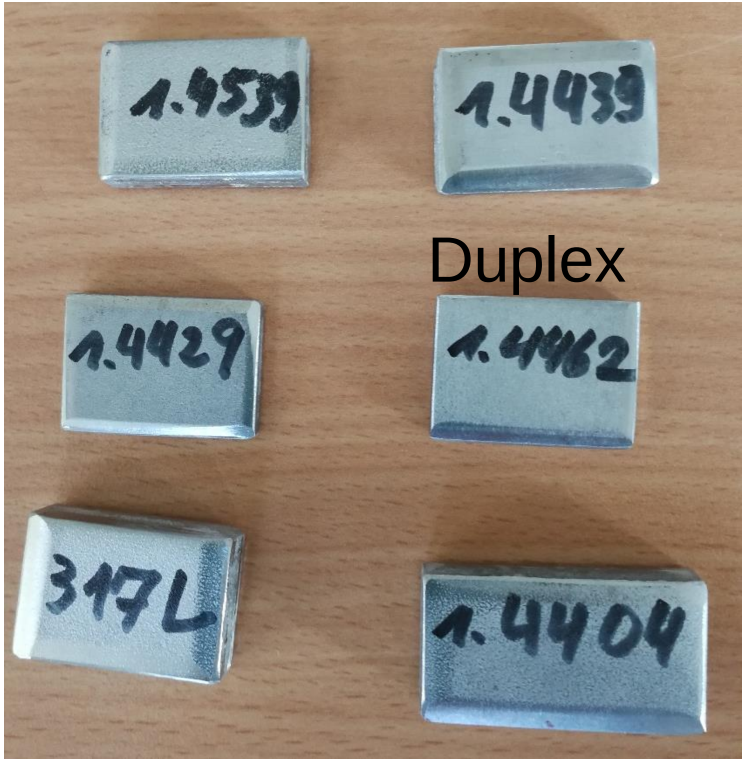
www.butting.com

Tests of cladding materials in autoclaves:

150° C, 1 mM Cu, 1.5 M $CaCl_2$, 2 M NaCl

- 5 Austenitic steel
- 1 Duplex
- Titanium
- C-steel (St37)

(5 Austenitic steel and 1 Duplex:) Used for cladding



Dauer	Werkstoff: **Titan 3.7035**
1 Monat	

Results

C-Stahl

24 h

7 days

Austenites and Duplex

→ Reaction of Cu^{2+} with C-Steel increases over time

→ Highly alloyed steels are corrosion resistant (slight crevice corrosion)

Outlook

Groß Schönebeck: → Need of pipe and casing materials resistant against electrochemical corrosion with Cu^{+}, Cu^{2+}

e.g. cladded pipes

Thank you

IFINKOR

Schmidt + Clemens

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Flowserve® Pumps

EBRO ARMATUREN®

BAM
Bundesanstalt für Materialforschung und -prüfung

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aufgrund eines Beschlusses des Deutschen Bundestages

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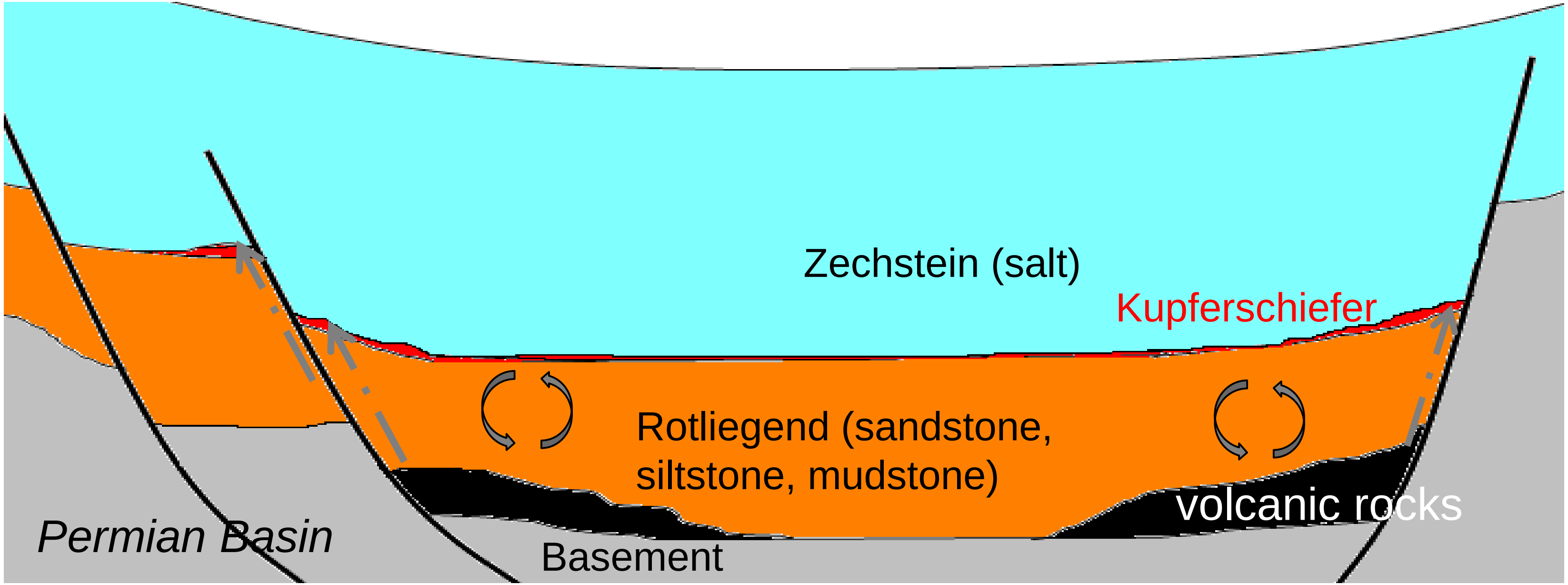
Woher stammt das Kupfer im Rotliegend?

1. Vulkangesteine als Quelle der Schwermetalle(Cu, Pb, Hg, Zn)
2. Auslaugung der Schwermetalle durch salinare Rotliegendfluide entlang Störungszonen (Bildung von Chloridekomplexen)



Total removed amount of solids (filter, bailer, well cleaning): ~ 600 L

Mean composition of all samples: