H2STORE HyINTEGER

H2STORE and HyINTEGER – studies on the effect of hydrogen storage in (PORE) underground gas reservoirs – an overview

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& the H2STORE / HyINTEGER team

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H2STORE

HyINTEGER

- H2STORE –

Investigations on geohydraulic, mineralogical, geochemical and biogenic processes during hydrogen underground storage in depleted gas reservoirs

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H2STORE

08.2012 – 12.2015

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- HyINTEGER –

Investigations on the integrity of wells and technical components exposed to high corrosive conditions in geological hydrogen underground reservoirs

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HyINTEGER

01.2016 – 12.2018

Supported by:
Federal Ministry for Economic Affairs and Energy
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Project consortium – 11 subprojects (6/5)

- 5 universities (plus 5 associated by contracts)

Institut für Geowissenschaften Jena · TU Clausthal · Université de Lorraine · Johannes Gutenberg Universität Mainz · HoME Hochschule Merseburg University of Applied Sciences

- 2 research centers

GFZ Helmholtz-Zentrum Potsdam · efzn Energie-Forschungszentrum Niedersachsen

- 4 cooperations with (international) R & D projects

Forschungsprojekt CO2MAN Pilotstandort Ketzin · ANGUS+ · Underground Sun.Storage · HYCHIC Diadema

- 5 industrial partners

uniper · E.ON Gas Storage · HYCHIC · VORWEG GEHEN · ENGIE by people for people · GDF SUEZ E&P Deutschland GmbH · RAG.AUSTRIA.ENERGIE

Major topic of H2STORE

Improving the understanding of potential processes during H_2-storage in depleted gas reservoirs, including their impact on:

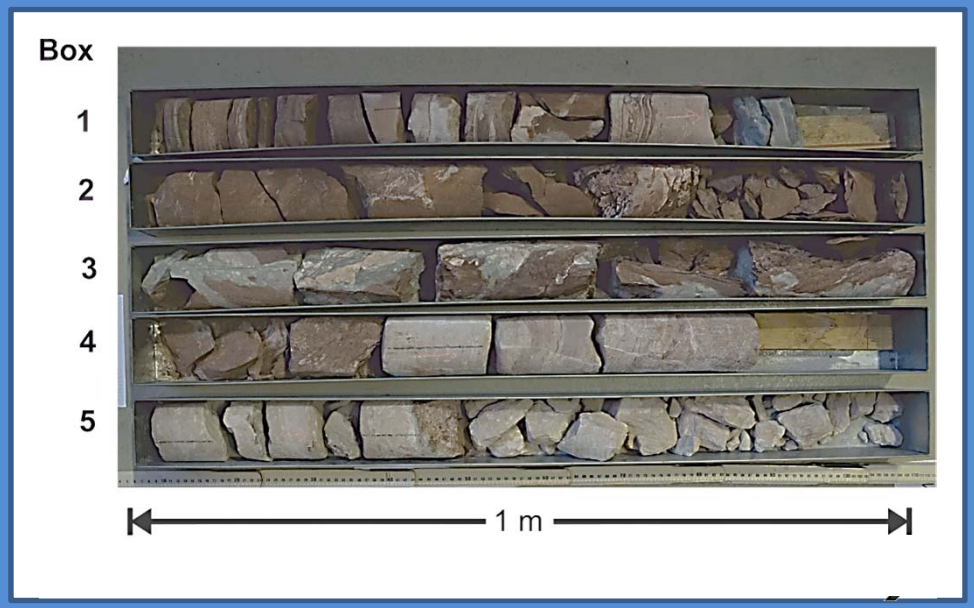
- long term capacity of the reservoir
- biocoenosis (variations in species and population growth)
- gas mixture behaviour
- fluid transport
- reactivity of the reservoir rocks

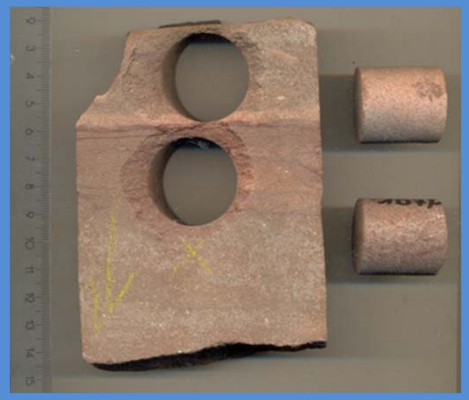
Major topic of Hy INTEGER

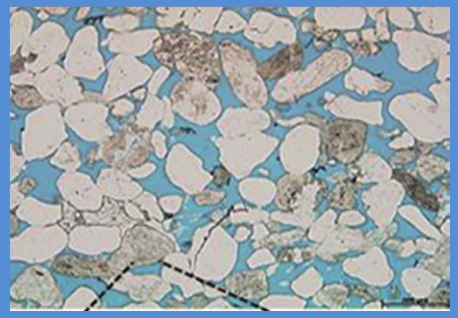
Improving the understanding of potential processes during H_2-storage *(and gas mixtures)* in depleted gas reservoirs *and well casing components*, including their impact on:

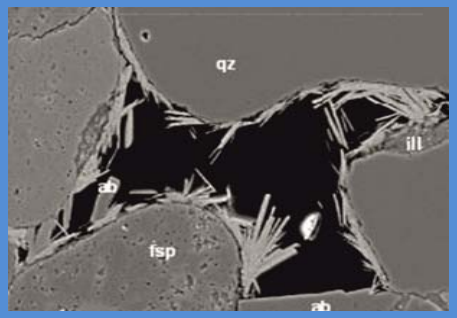
- alteration of steel alloys, well cements, and elastomers (in combination with the reservoir rocks/fluids)
- the integrity of the reservoirs (caprock and well leckage)
- reactivity of the components – e.g. variations caused by different gas mixtures (e.g. H_2-CO_2, H_2-CH_4, H_2-H_2S, H_2-$C_2H_4O_2$) and in the order of their addition to the samples
- gas mixture behaviour and fluid transport

Material

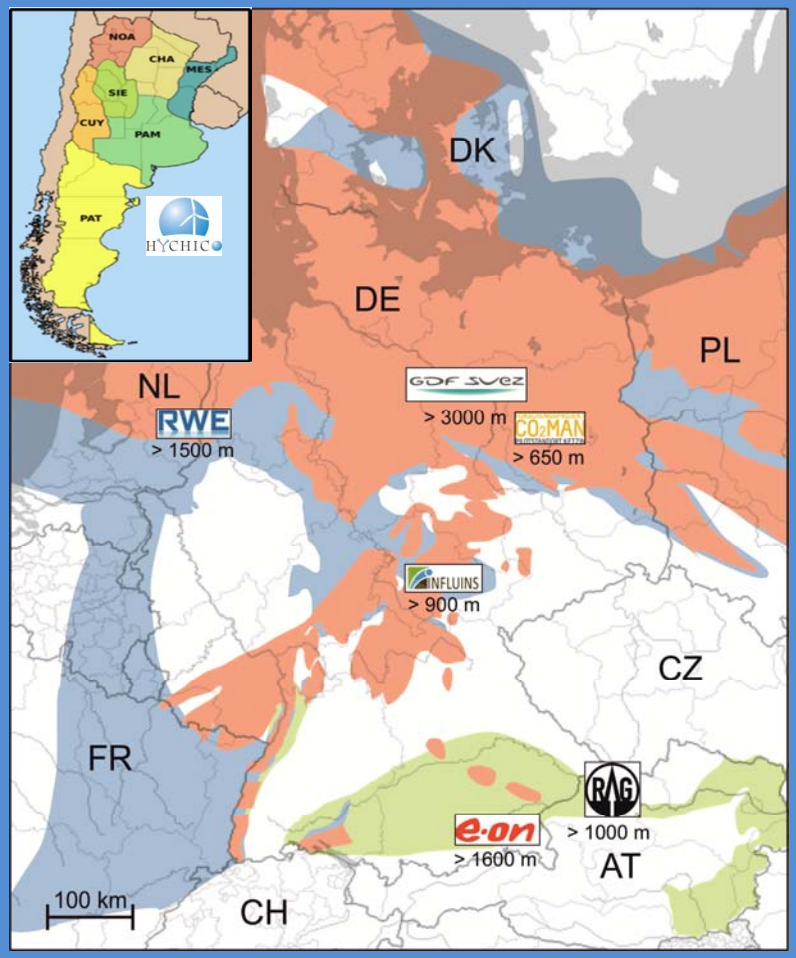






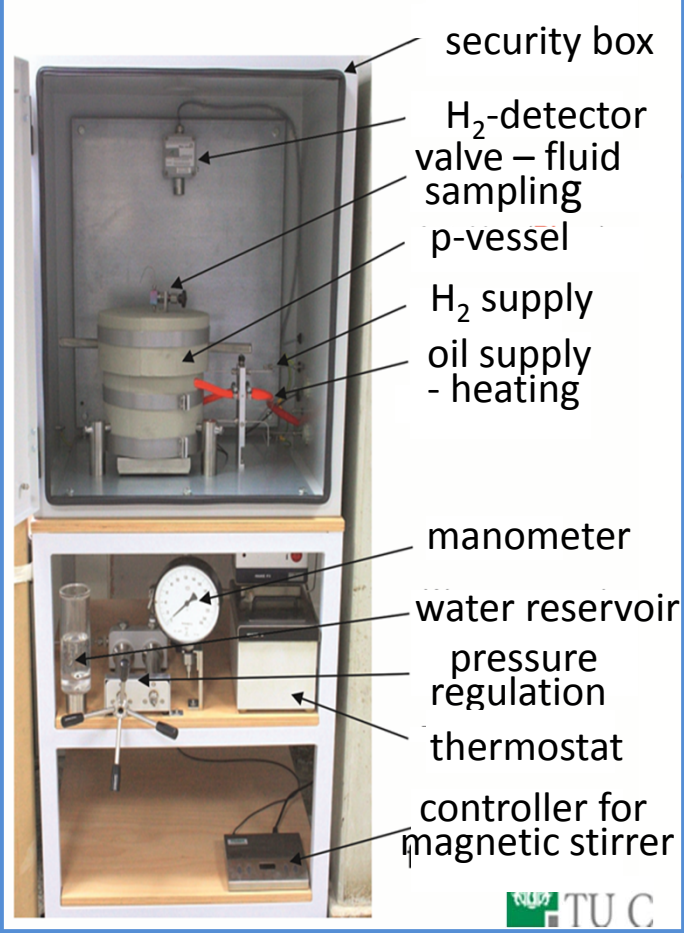


Locations



Age:
~ 25 – 270 Ma (Tertiary – Permian)
Depths:
~ 700 – 3.500 m
Pressure:
~ 4 – 20 MPa
Temperature:
~ 40 – 125°C
Rock type:
(sub-)arkoses – feldspathic litharenites
Salinity of formation fluids:
~ 350 – 10 g/l

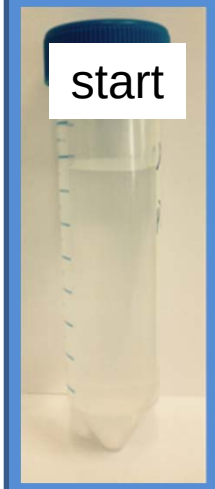
Experimental set-up

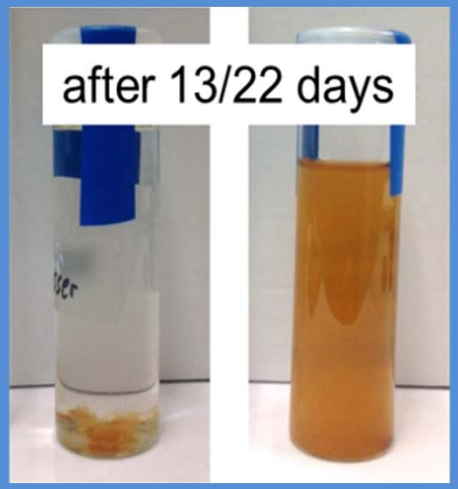


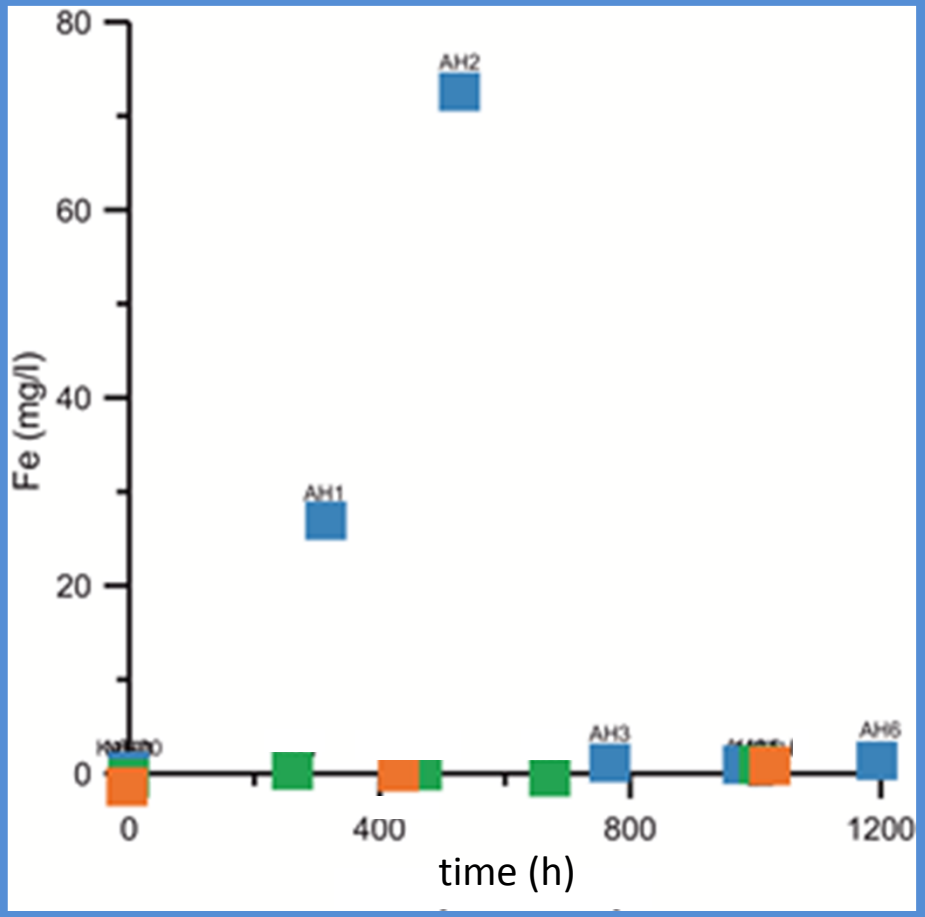
Left: autoclave system at the University Clausthal – static conditions: p = max. 20 MPa, T = max. 120°C for 4 – 6 weeks, **pure (100%) H_2**

Below: cylinders, p = 10 MPa, T = 25°C for 1 – 2 weeks, **100 % H_2** – only rock powder

Corrosion of steel alloys (1)







Corrosion of steel alloys (2)

Alloys:

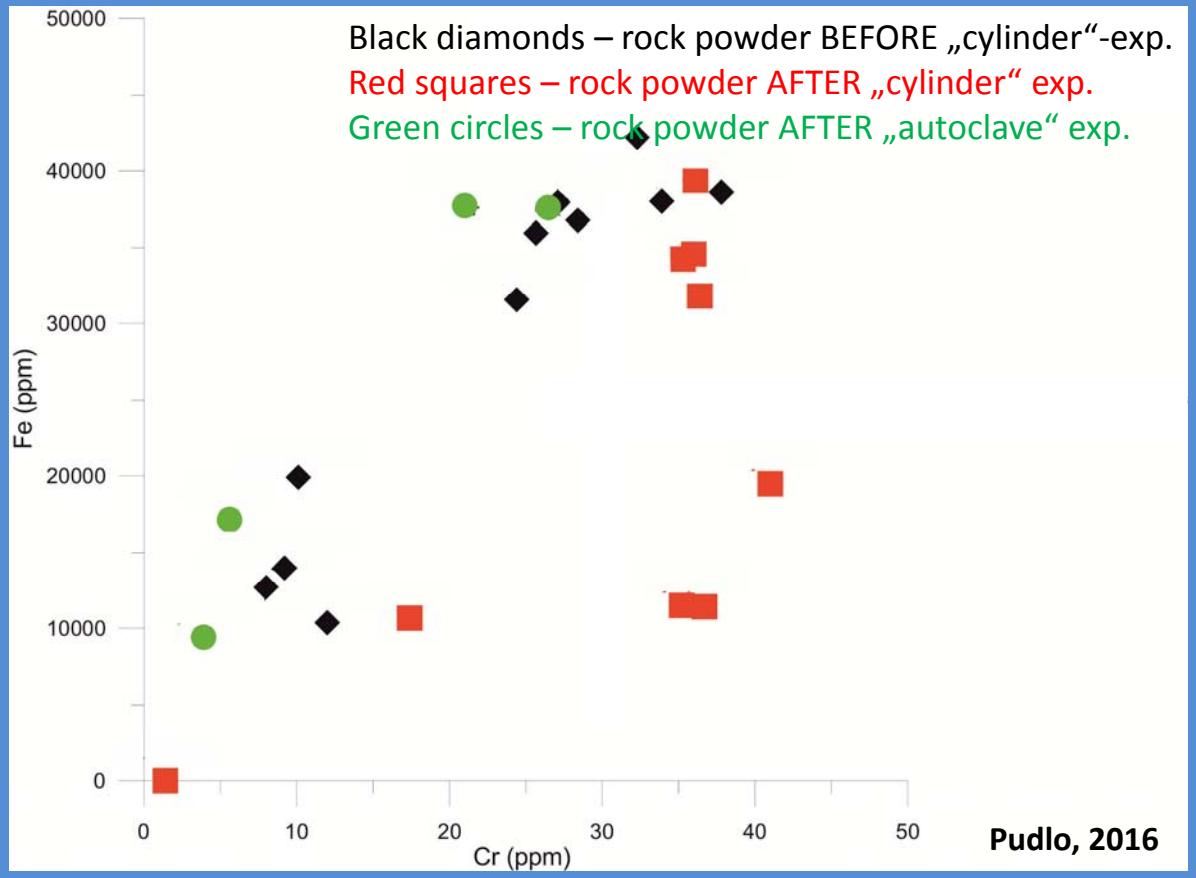
Autoclave – Steel no. 1.4404

Ni – 10.12%, Cr – 16.88%, Fe – max. 68.8%

Valve for fluid sampling – Steel no. S 316

Ni - 10-14%, Cr – 16-18%, Fe – 61.8-72%

Corrosion of steel alloys (3)



Steel no. S 316L

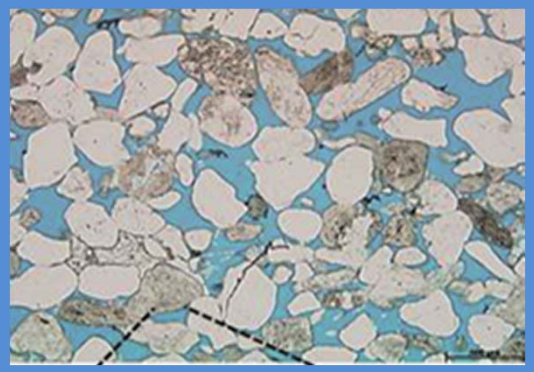
Element	Min	Max
C	-	0,035
Mn	-	2
Ni	10	15
Cr	16	18
Mo	2	3
S	-	0,03
Si	-	1
P	-	0,045
(Fe	60,89	72)

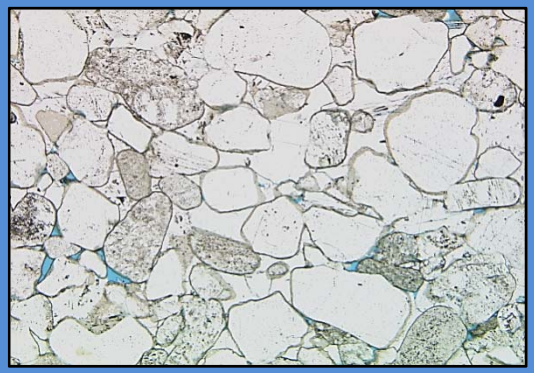
Rate in corrosion of steel alloys

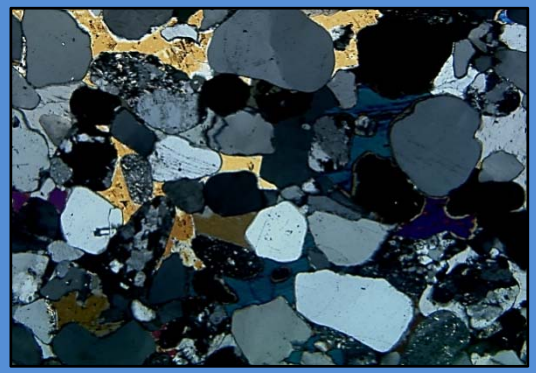
Kind of alloy Used for	316 (L) tube of valve (autoclave) & cylinders	1.4404 autoclave (vessel)	C-276 (Hastelloy) autoclave (valve)
COMPOSITION			
Ni (%)	10 – 15	10.12	51.1 – 62.9
Cr (%)	16 – 18	16.88	15.0 – 16.5
Fe (max. - %)	72	68.88	4.0 – 7.0
Mo (%)	~ 1	2.00	15.0 – 17.0

Corrosion of steel alloys (4)

– what are potential reasons for this alteration (H_2S) ?







(a) pyrite alteration (rare, but pH relevant)

- at lower pH values (pH < 6,8):

pyrite (FeS_2) + hydrogen = **H_2S**

- at alkaline conditions (pH ~ 6,8–10):

pyrite + hydrogen = pyrrhotine (FeS) + **H_2S**

(Allan et al. 2011; Truche et al., 2010)

(b) sulfate reduction (frequent)

$2H + CaSO_4 = Ca(OH)_2 + SO_2$

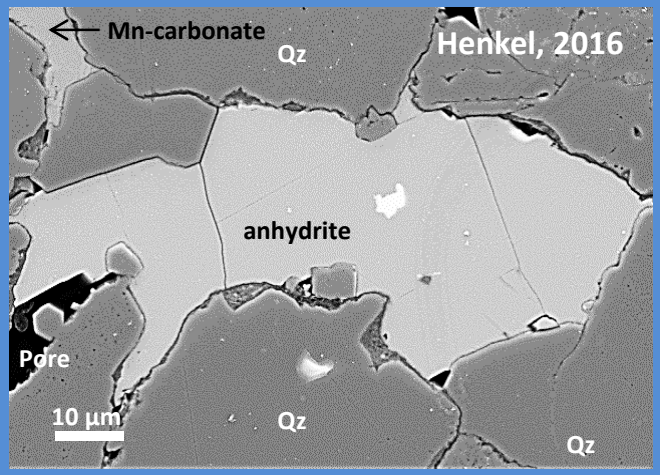
$2H + SO_2 = SO + H_2O$

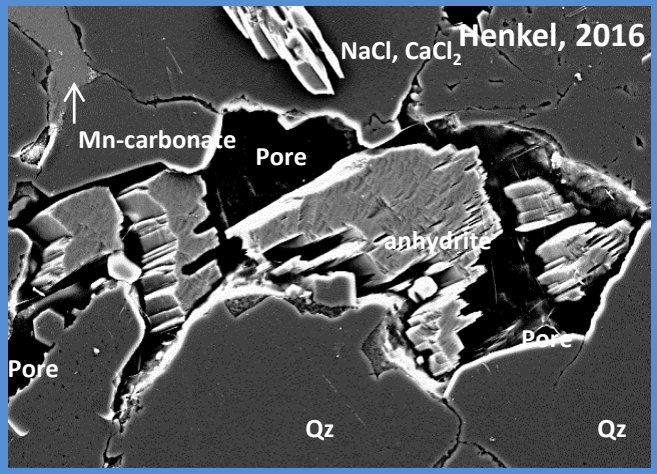
$2H + SO = S + H_2O$

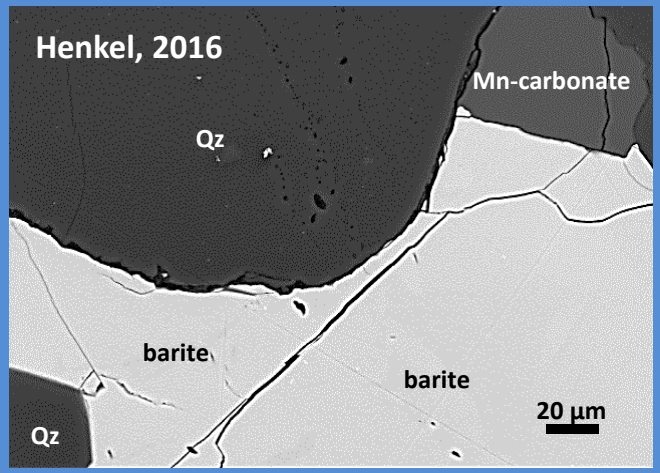
$2H + S = $ **H_2S**

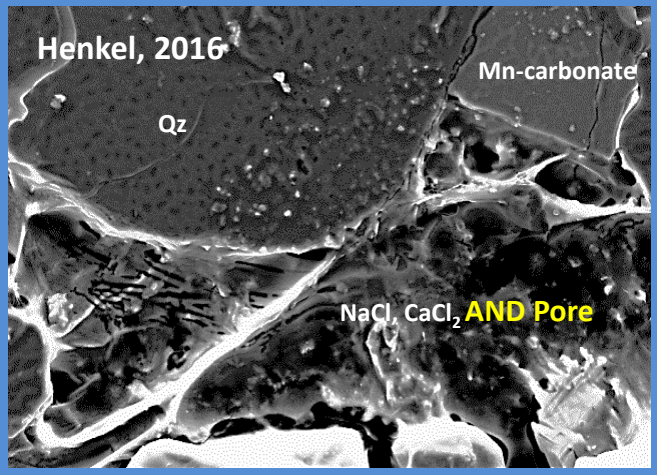
(Anisimov, 1978)

Sulfate dissolution observed: anhydrite ($CaSO_4$) and barite ($BaSO_4$)

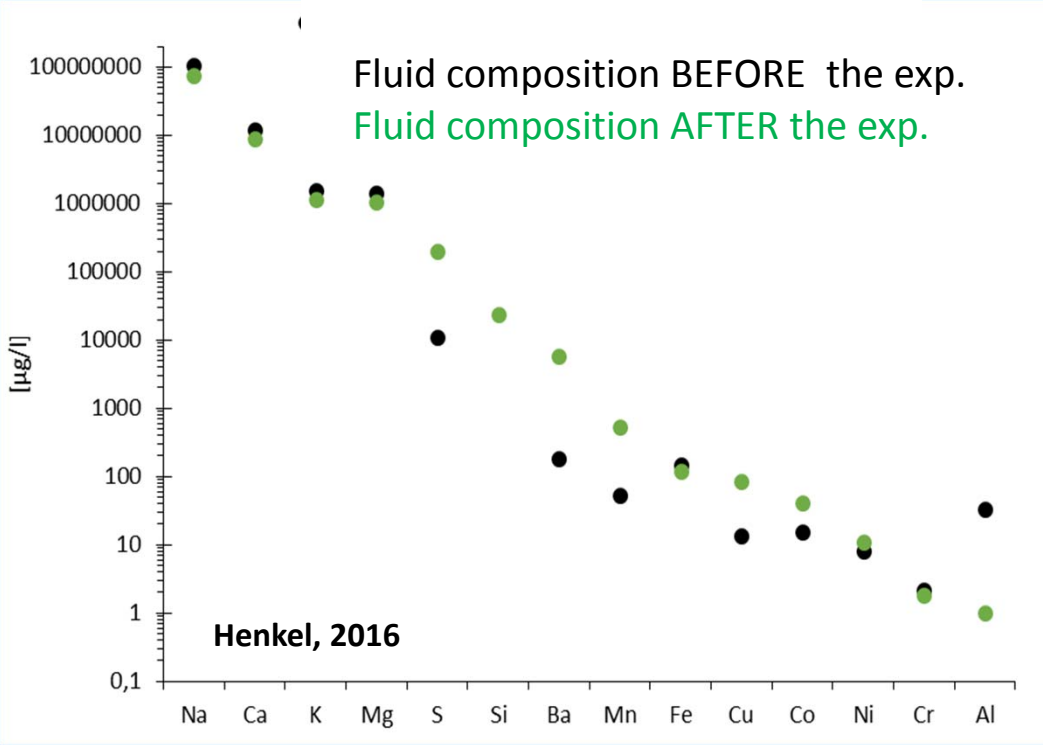


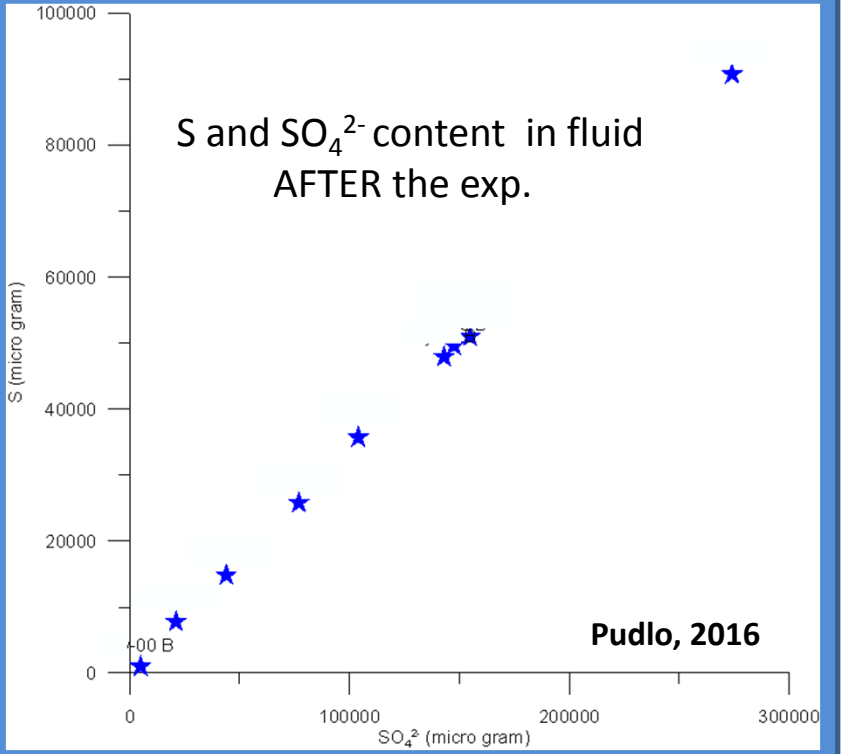




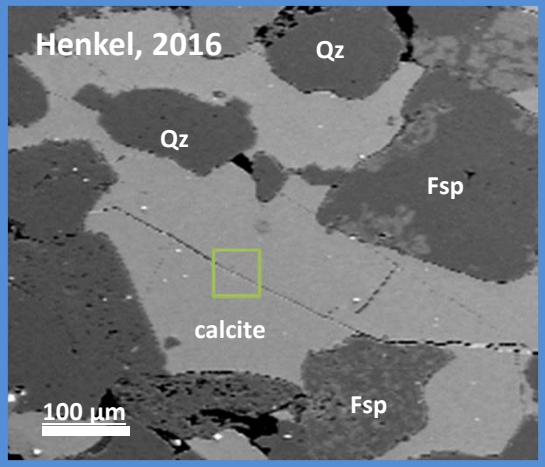


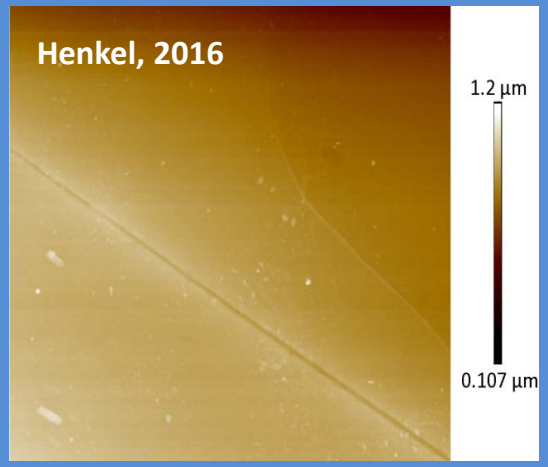
Sulfate dissolution proven by chemical means

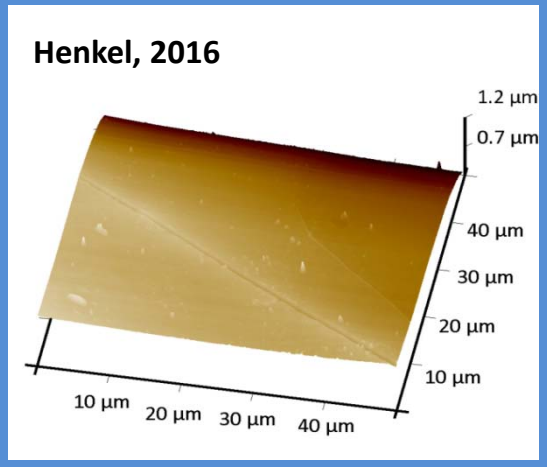


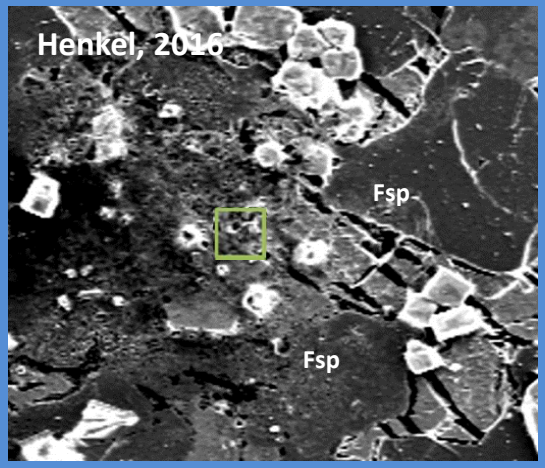


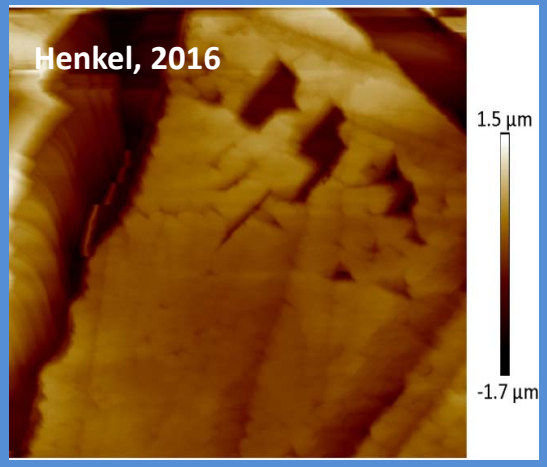
NOT ONLY sulfate, but also calcite dissolution is proven

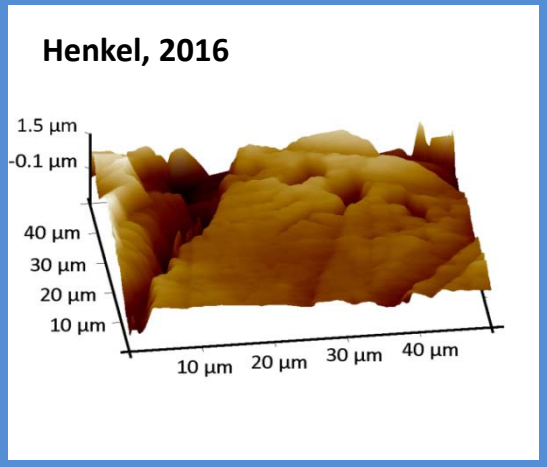




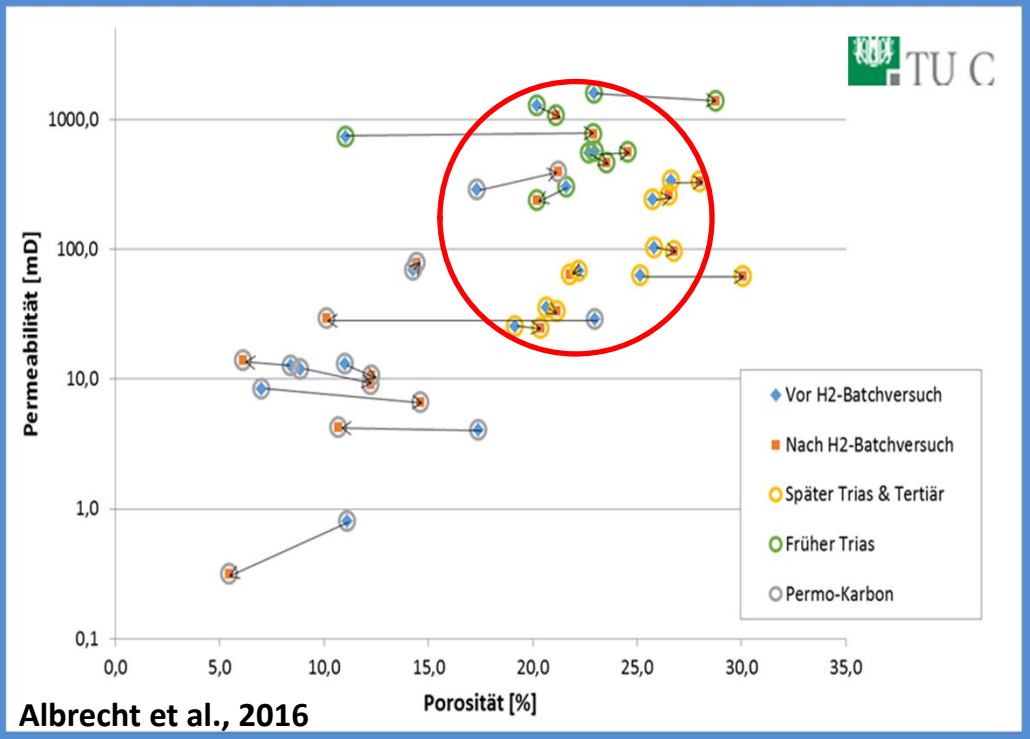




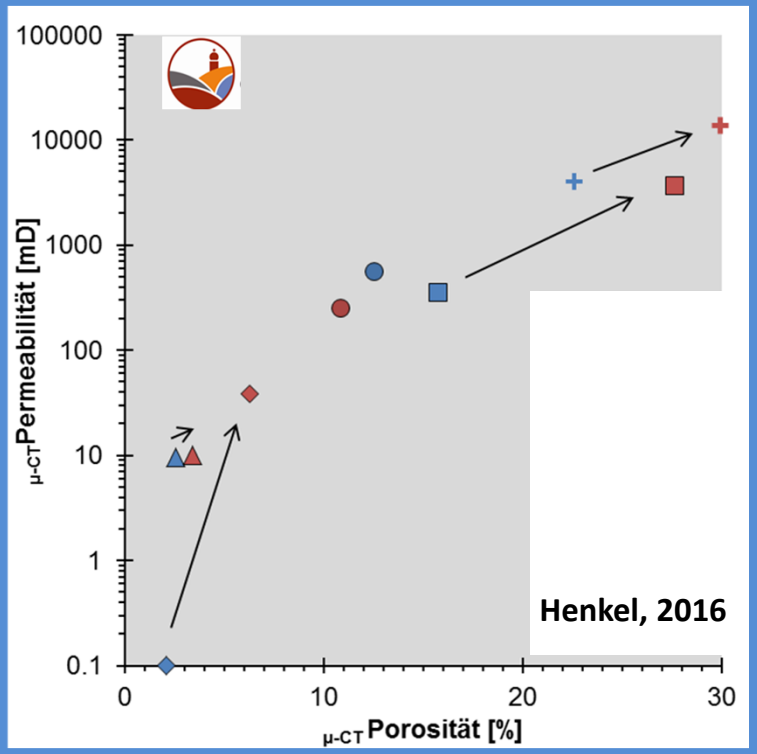




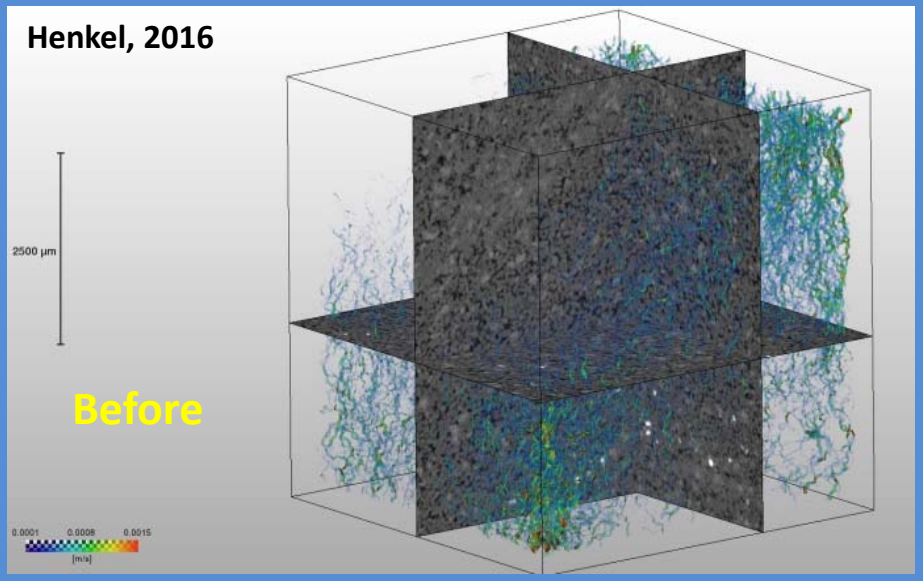
Mineral reactions and their relevance to reservoir quality

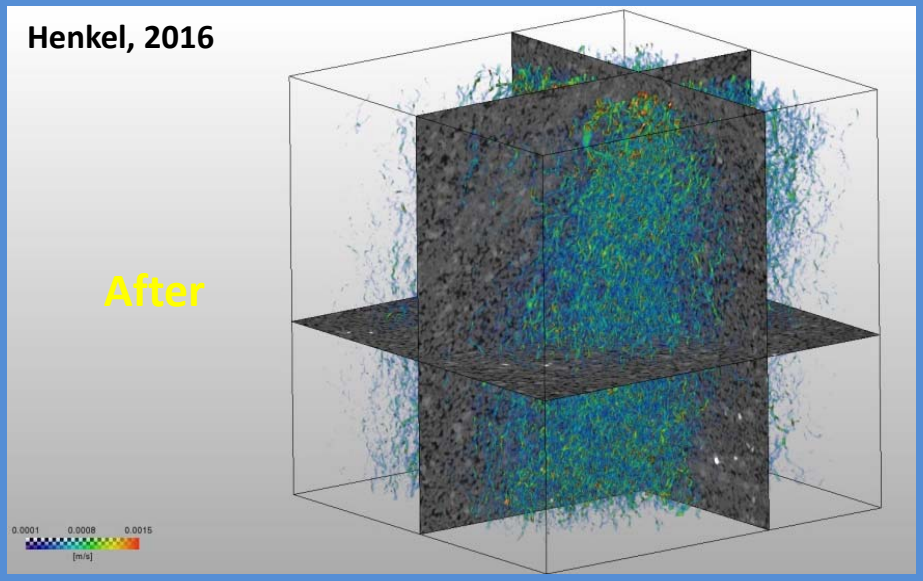


Albrecht et al., 2016



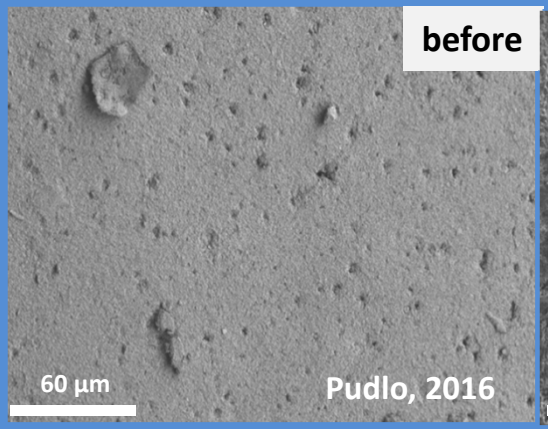
Relevance of porosity and permeability on fluid flow

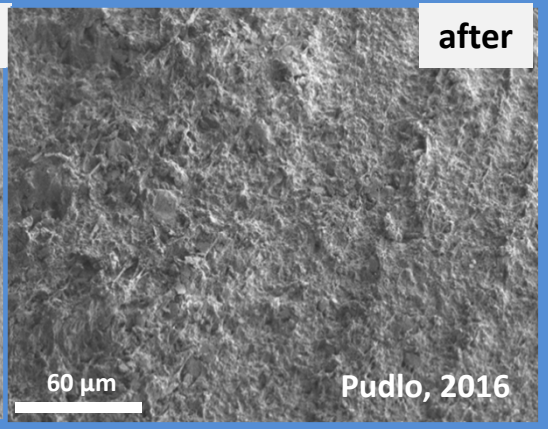


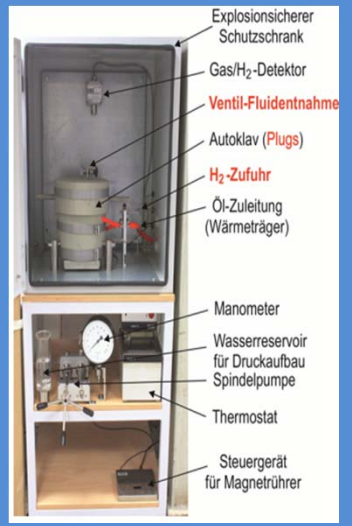


After the experiments porosity increases and fluid flow is enhanced - due to the dissolution of (formerly) pore-filling carbonate and sulfate cements.
Blue colours refer to low, red colours to high fluid flow velocities

Alteration of elastomers/sealing components (= packers)







<u>Also:</u> alteration of glass is observed - not (?) relevant to storage

Summary and Outlook

1. Sulfates and calcite are major components of well cements – further research on the fate of other carbonate species is planned
2. Steel alloys exposed to **pure (100 %) H_2** differ in their corrosion rate
3. Mineral (as well as steel corrosion) reactions **differ in a site specific way** (high salinity vs. low salinity and T-p)
4. Alteration-/mineral dissolution processes will modify reservoir quality and thus storage capacities and recovery rates
5. The alteration of elastomers/sealing components (e.g. “packers”) is reasonable, which might result in some leakage of the well
6. Planned H_2-CH_4 experiments are in context with H_2-pipeline storage and storing such gas mixtures in large-scale underground reservoirs
7. This research is not only relevant for H_2-storage, but also for almost every HC-wells and for cavern storage operations

H2STORE ENERGIESPEICHER Forschungsinitiative der Bundesregierung Hy INTEGER

Thank you for your attention !

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