Effects of CO_2 impurities on storage

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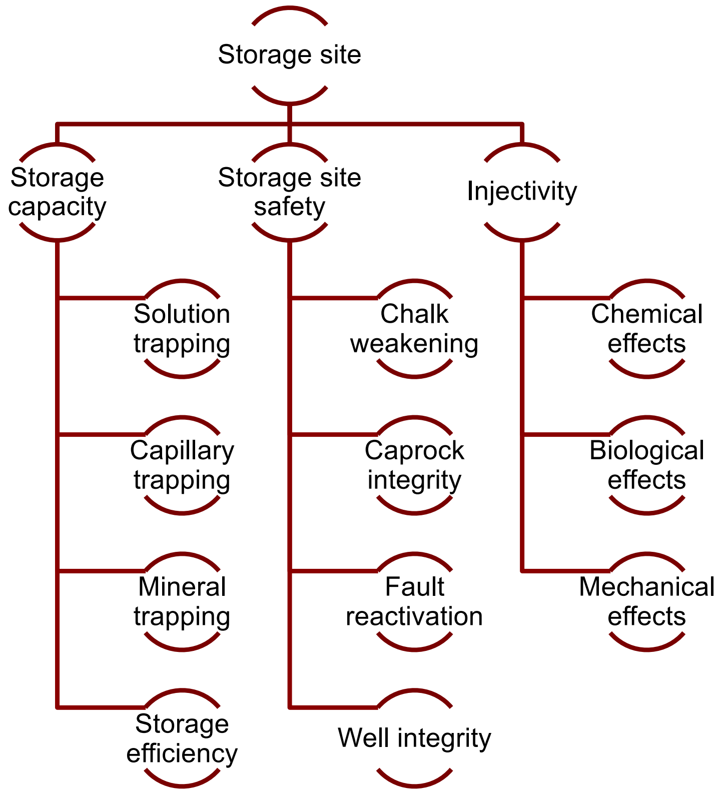
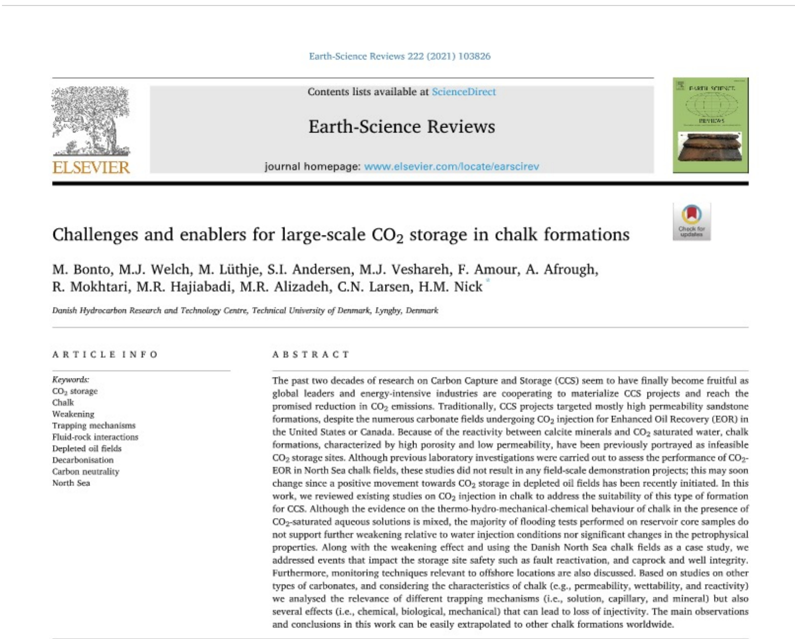
CO_2 Storage – State of the Art Study





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Challenges and enablers for large-scale CO_2 storage in chalk formations

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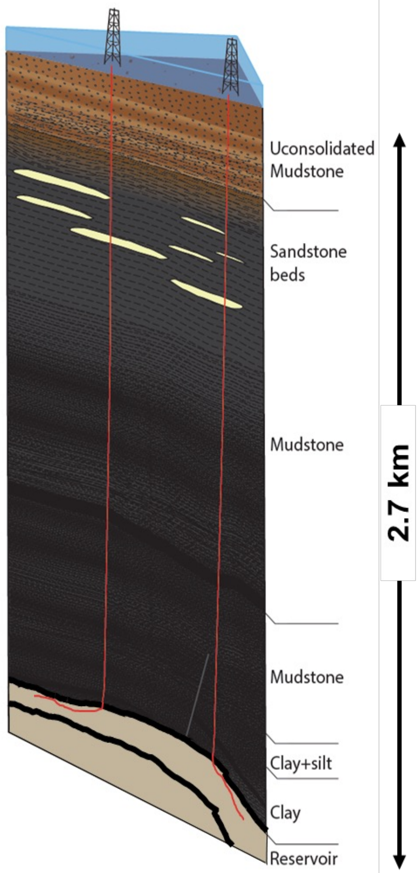
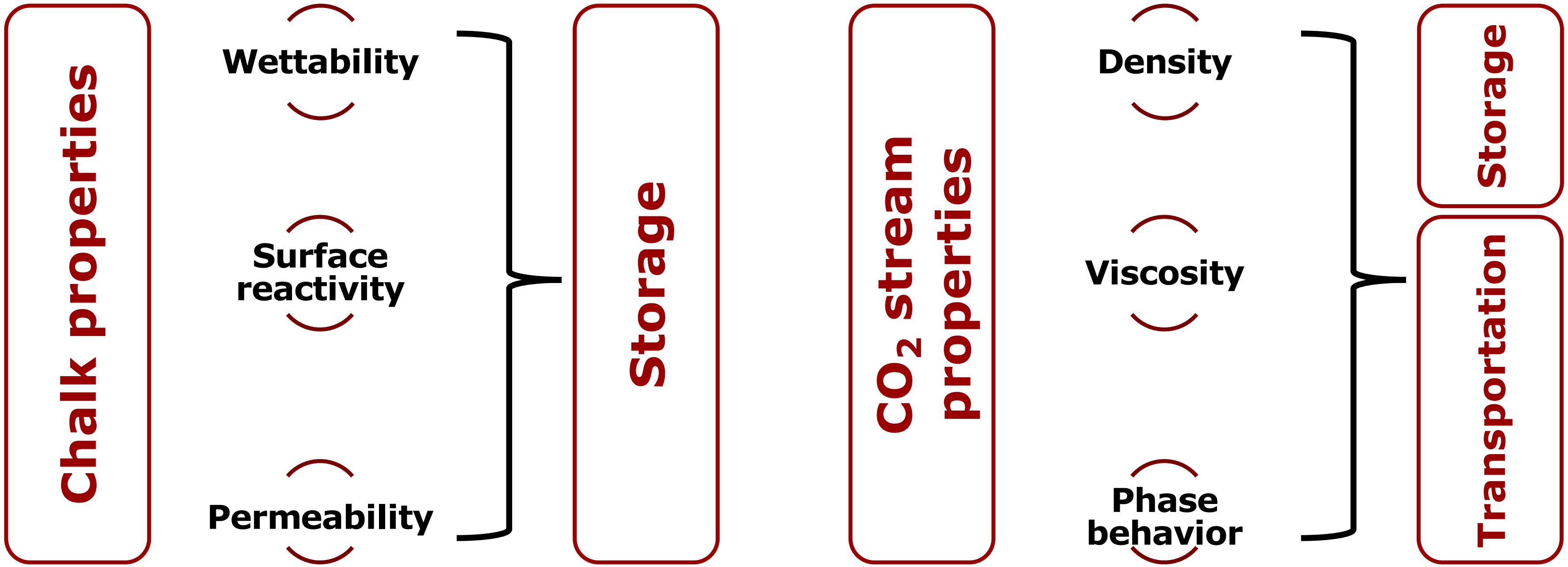
ABSTRACT

The past two decades of research on Carbon Capture and Storage (CCS) seem to have finally become fruitful as global leaders and energy-intensive industries are cooperating to materialize CCS projects and reach the promised reduction in CO_2 emissions. Traditionally, CCS projects targeted mostly high permeability sandstone formations, despite the numerous carbonate fields undergoing CO_2 injection for Enhanced Oil Recovery (EOR) in the United States or Canada. Because of the reactivity between calcite minerals and CO_2 saturated water, chalk formations, characterized by high porosity and low permeability, have been previously portrayed as infeasible CO_2 storage sites. Although previous laboratory investigations were carried out to assess the performance of CO_2-EOR in North Sea chalk fields, these studies did not result in any field-scale demonstration projects; this may soon change since a positive movement towards CO_2 storage in depleted oil fields has been recently initiated. In this work, we reviewed existing studies on CO_2 injection in chalk to address the suitability of this type of formation for CCS. Although the evidence on the thermo-hydro-mechanical-chemical behaviour of chalk in the presence of CO_2-saturated aqueous solutions is mixed, the majority of flooding tests performed on reservoir core samples do not support further weakening relative to water injection conditions nor significant changes in the petrophysical properties. Along with the weakening effect and using the Danish North Sea chalk fields as a case study, we addressed events that impact the storage site safety such as fault reactivation, and caprock and well integrity. Furthermore, monitoring techniques relevant to offshore locations are also discussed. Based on studies on other types of carbonates, and considering the characteristics of chalk (e.g., permeability, wettability, and reactivity) we analysed the relevance of different trapping mechanisms (i.e., solution, capillary, and mineral) but also several effects (i.e., chemical, biological, mechanical) that can lead to loss of injectivity. The main observations and conclusions in this work can be easily extrapolated to other chalk formations worldwide.

https://doi.org/10.1016/j.earscirev.2021.103826



CO2 Storage – State of the Art Study



Impurities in the CO2 stream impact the storage in the subsurface

DTU

CO2 stream composition

The composition of the CO_2 stream depends on the fuel, source, and capture method

CO2 quality - recommendations

DYNAMIS project (*Towards Hydrogen and Electricity Production with CCS*) (2006-2009)

de Visser et al., 2008 (IJGGC)

Component	Composition	Limitation
CO2	>95.5%	
H2	<4% *	H&S
Ar	<4%*	ENCAP
N2	<4%*	ENCAP
CH4	<4% vol. (aquifer), <2% vol (EOR)	ENCAP
CO	2000 ppm	H&S
H2S	200 ppm	H&S
H2O	500 ppm	D&O

D&O – Design and Operational
H&S – Health and Safety
ENCAP (*Enhanced Capture of CO2*) (2004-2009)
*Sum of concentrations of non-condensable gases to be kept >4%

CO_2 quality recommendations represent a trade-off between the compositional requirements along the entire CCS value chain

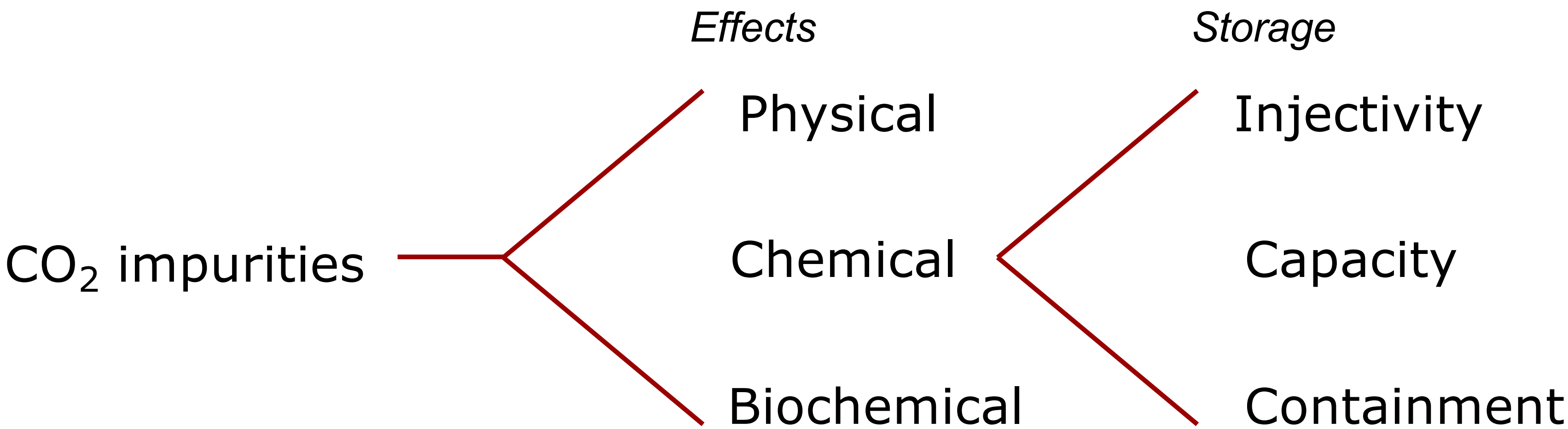
CO_2 quality - materialized

CO_2 stream composition used in the Aramis project

Component	Composition [mole %]
CO2	95
H2O	0.004
N2	2
O2	0.004
H2	0.75
He	1
Ar	1
CH4	7.5×10^{-2}

Component	Composition [mole %]
CO	5.0×10^{-4}
H2S	3.0×10^{-4}
NO2	2.0×10^{-4}
NO	5.0×10^{-3}
SO2	1.2×10^{-1}
C2H6	3.5×10^{-2}
CH4O	2.0×10^{-3}

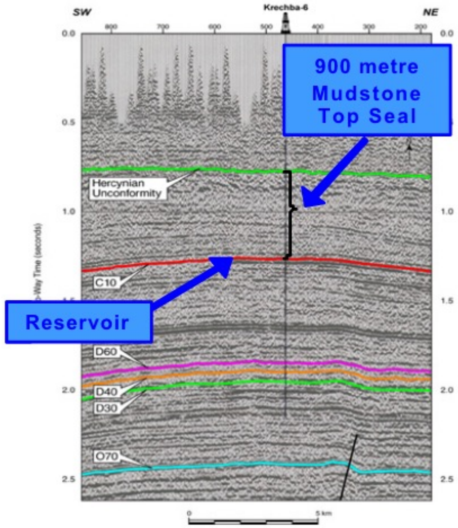
Impact of impurities on the storage



The impact of impurities in captured CO_2(from power plants and other CO2-intensive industries) on CO_2 transport and storage was assessed in the **IMPACTS** collaborative project. (2013-2016)

Type of storage

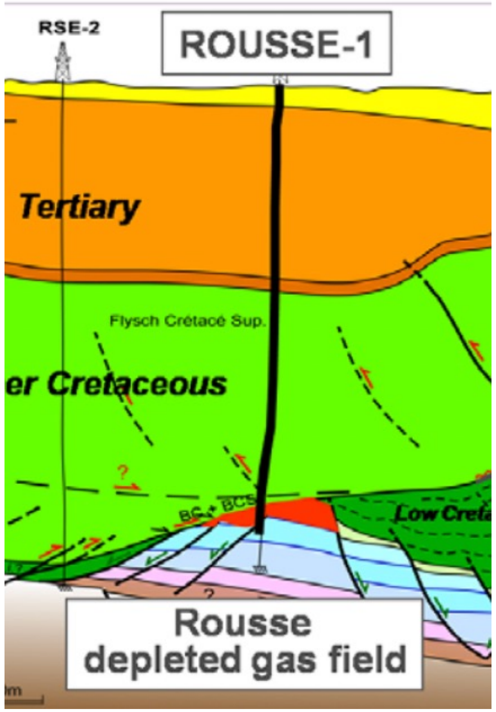
In Salah



Mathieson, A., et al. 2011.

Saline aquifers

Lacq CCS project



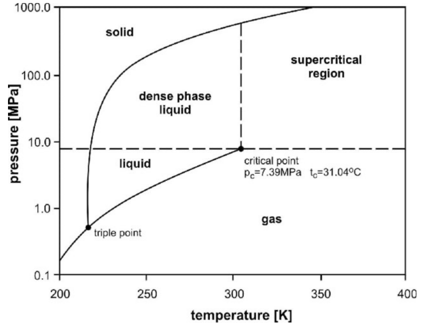
Lescanne, Marc, et al. 2011

Depleted HC reservoirs

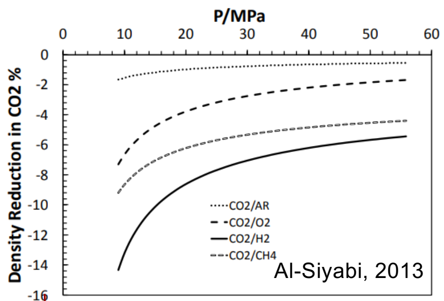
Physical effects

- Impurities induce changes in:

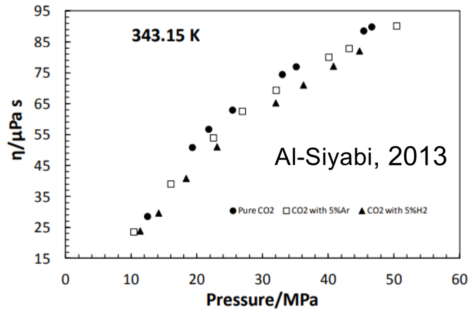
Phase behavior



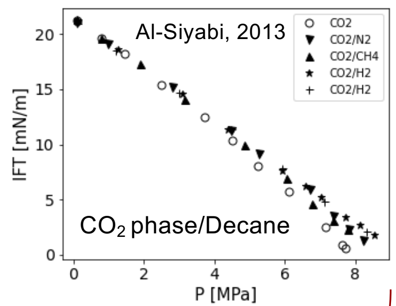
Density



Viscosity

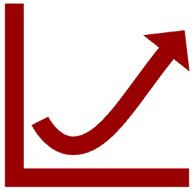


IFT



Experimental measurements on binary systems

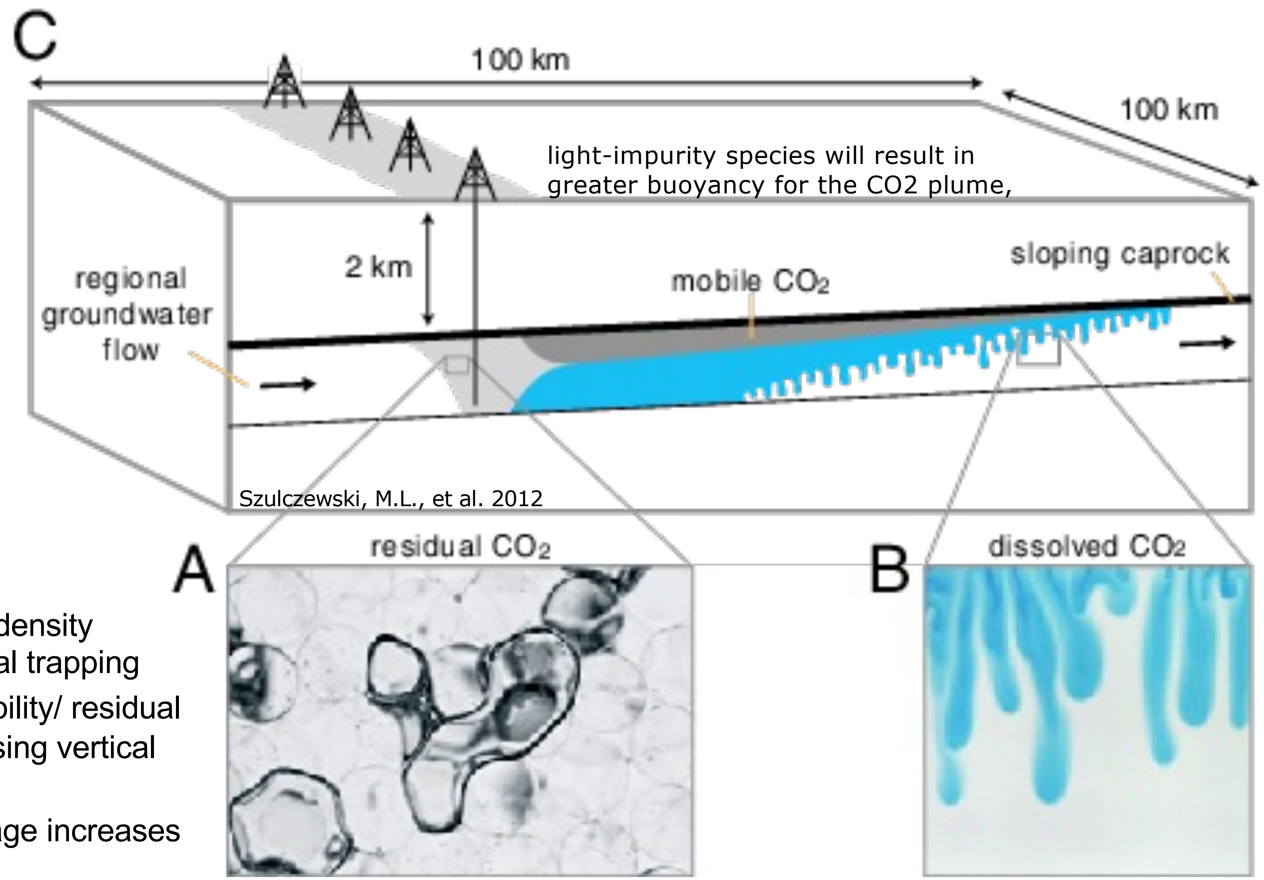
$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)+b(V-b)}$$

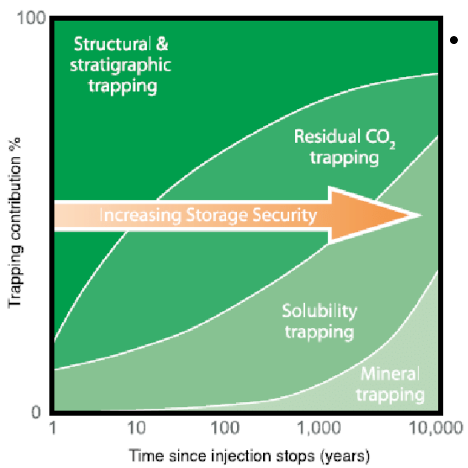


Predict the physical behavior of CO_2 streams with complex composition at different P,T

Physical effects

Storage mechanisms





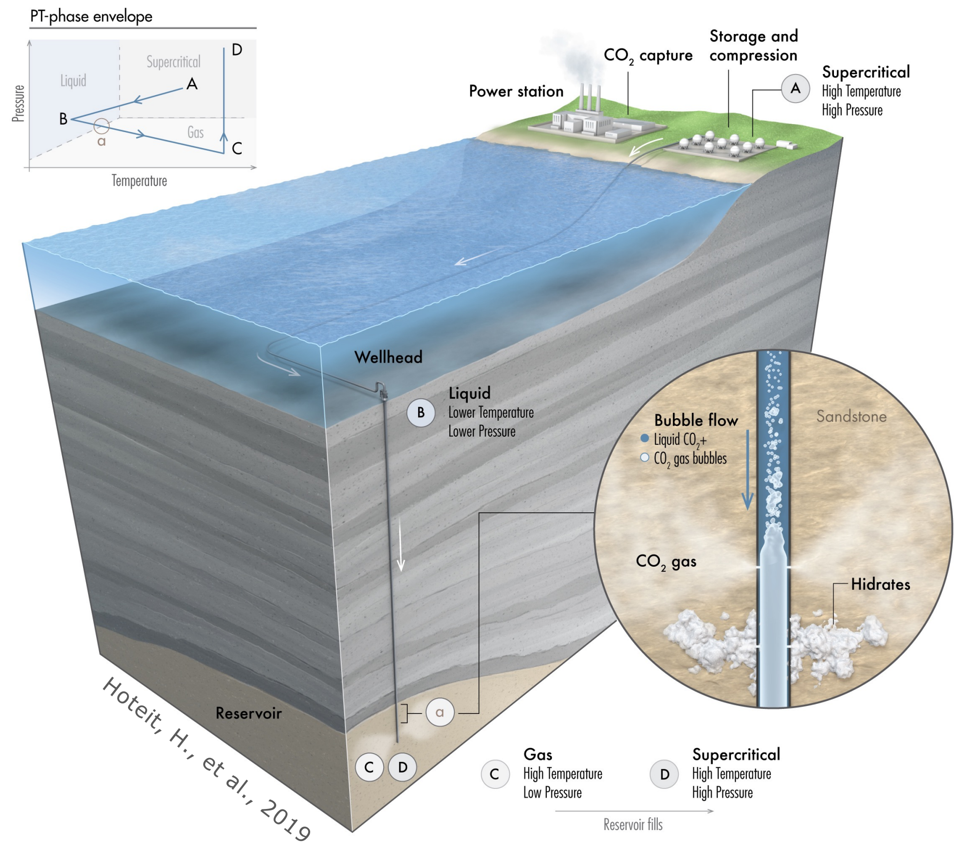
- Reduced CO2 mixture density results in more structural trapping
  - less time for solubility/ residual trapping due to rising vertical velocity
  - potential for leakage increases

- Increase of IFT will increase capillary trapping

- Reduced convective fingers due to less increase of water density
- Reduced solution trapping

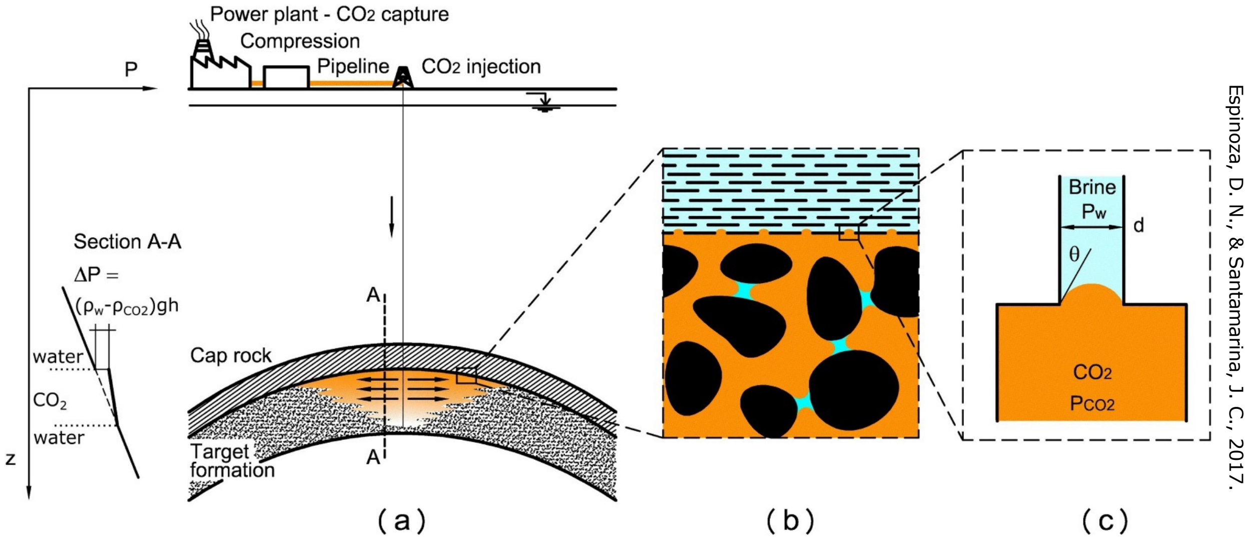
Physical effects – Injectivity

- Decreasing viscosity increases the mass flux for the same pressure drop
- Increasing density decreases the mass flux



Hoteit, H., et al., 2019.

Physical effects – membrane seal



$$\text{conversion factor} = \frac{\Delta\rho_{hydrocarbon/water}}{\Delta\rho_{CO_2/water}} \frac{\cos\theta_{CO_2/water}}{\cos\theta_{hydrocarbon/water}} \frac{\sigma_{CO_2/water}}{\sigma_{hydrocarbon/water}}$$

Chemical effects

Dissolution of CO2/impurities in FW

- Some impurities have a higher solubility in FW compared to CO2

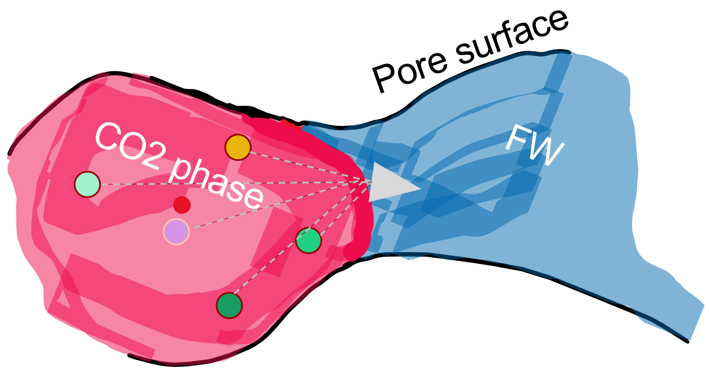
pH decrease

- Dissolved impurities can drive pH to lower values compared to carbonic acid

Dissolution/precipitation reactions

- E.g., calcite dissolution, anhydrite precipitation

Changes in porosity/permeability



- Synergistic chemical effects of impurities:
  - O2 can oxidize some of the impurities

$$H_2S(g) + 2O_2\ (g)\ \rightarrow SO_4^{2-}(aq) + 2H^+(aq)$$
$$2NO(g) + 2O_2\ (g)\ \rightarrow 2NO2\ (g)$$

  - H2S and SO2 can lead to the formation of sulfur

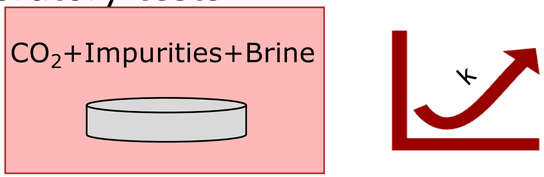
$$2H_2S\ (g) + SO_2\ (g)\ \rightarrow 3S\ (s) + 2H_2O$$

Impurities in the CO2 stream can also undergo chemical reactions with the cement barrier or increase well corrosion rates

Chemical effects

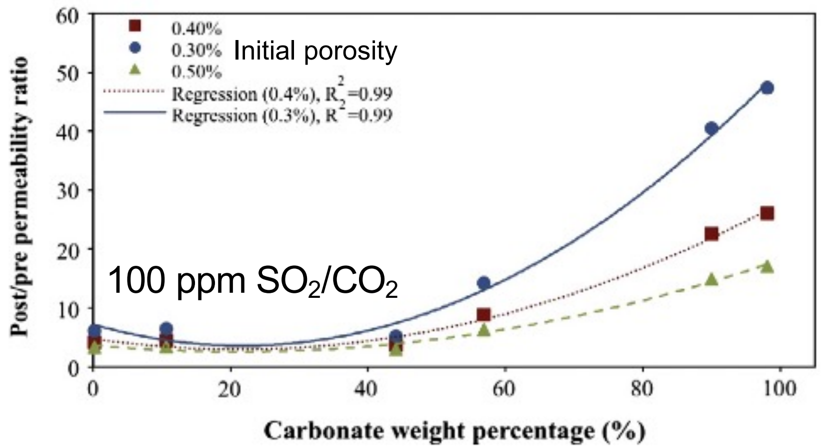
❑ Pilot tests
- Hontomin (tight carbonates): 95% CO_2/ 5% synthetic air
- Ketzin (sandstone): 80% CO_2/ 20%N_2

❑ Laboratory tests



- Sandstones: no/minimal alteration of permeability/porosity alteration after soaking
- Change in permeability of caprocks dependent on impurity and carbonate content

❑ Long-term simulations of CO_2 injection in sandstones aquifers generally show that long-term effect of impurities on the porosity/permeability is minor.



Bolourinejad, P., & Herber, R. (2015). *Applied Geochemistry*

In depleted oil fields, the presence of residual oil coating the mineral surface may limit the extent of geochemical reactions.

Chemical effects – Injectivity

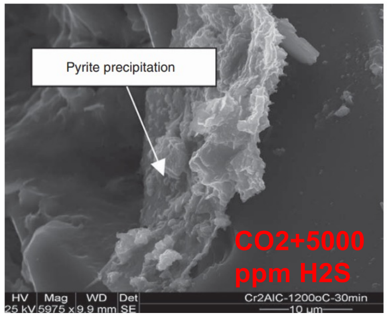
Injectivity

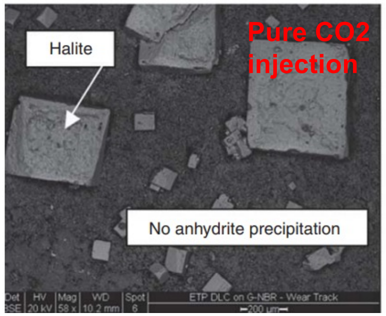
Mineral dissolution | … | … | … | … | **Salt precipitation**

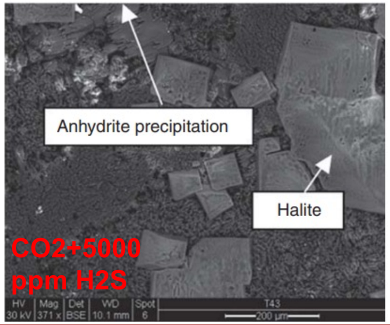
- The dissolution of CO_2 in brine decreases pH, promoting mineral dissolution
- Impurities soluble in water can decrease pH further leading to additional aqueous species
- Aqueous species stemming from impurities promote precipitation of secondary mineral phases

- CO_2/H_2O mutual solubility lead to a "drying out" effect
- Impurities can intensify water vaporization, promote the precipitation of secondary phases and further enhance salt precipitation

Bolourinejad, P., & Herber, R. (2014). *SPE Journal*



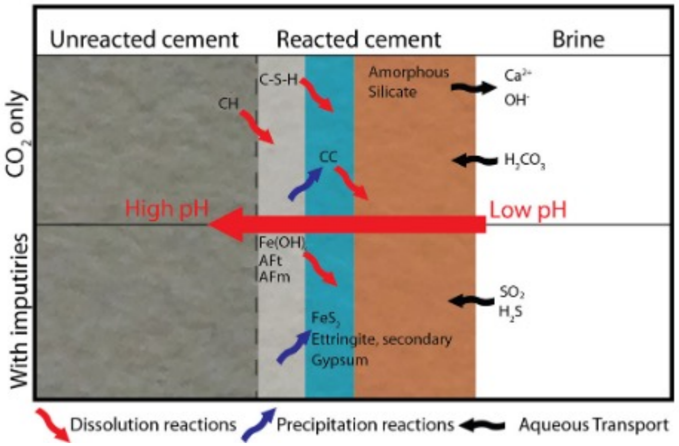




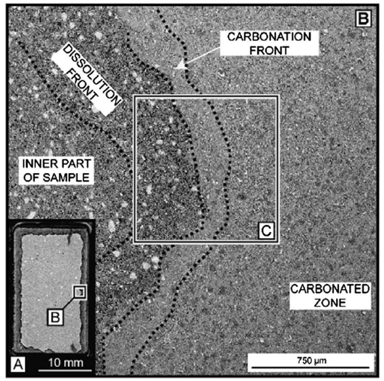
- Lower pH in the presence of H_2S did not decrease the permeability → precipitation of secondary phases (e.g., pyrite, anhydrite)

Chemical effects – Containment

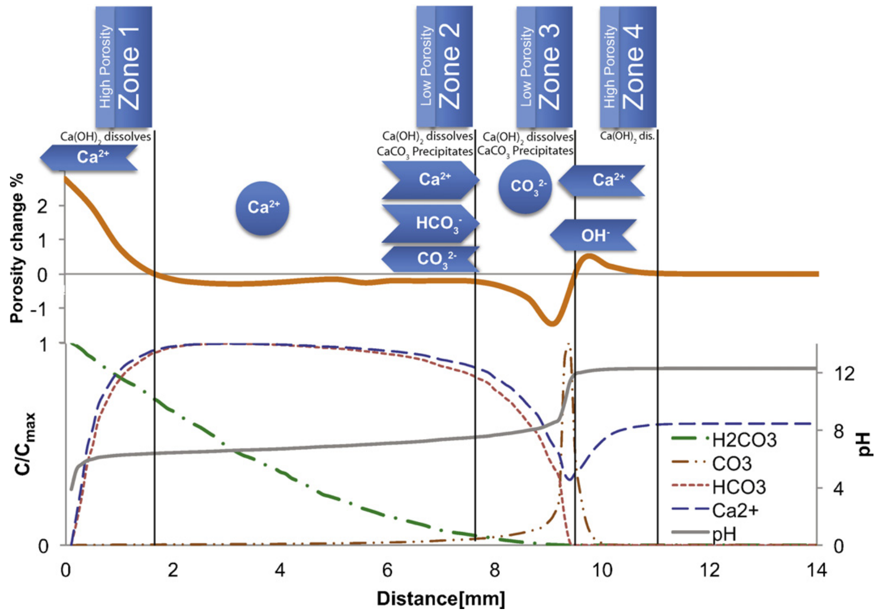
Carroll et al., 2016



CH – Portlandite
C-S-H – Calcium-silicate-hydrate
CC – Calcium carbonate
AFm – Monosulfate
Aft – Trisulfate



Šavija, B., & Luković, M. (2016).



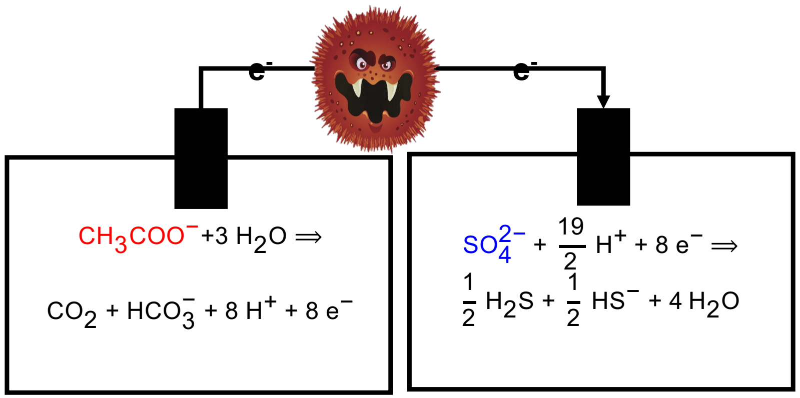
- H_2S and SO_2 drive additional interactions with the cement (oxidation-reduction, sulfidation)
  - Formation of secondary phases, e.g., ettringite, pyrite
- CO2/H2S (21% mol) did not induce mechanical damage on the cement
- Low impurity concentrations expected to have no major effect on the permeability of Portland cement

Raoof, A., Nick, H. M., Wolterbeek, T. K. T., & Spiers, C. J. (2012). *International Journal of Greenhouse Gas Control*

Biochemical effects

Life in the subsurface is controlled by electron transfer

Sulfate reducing microorganisms (SRM)

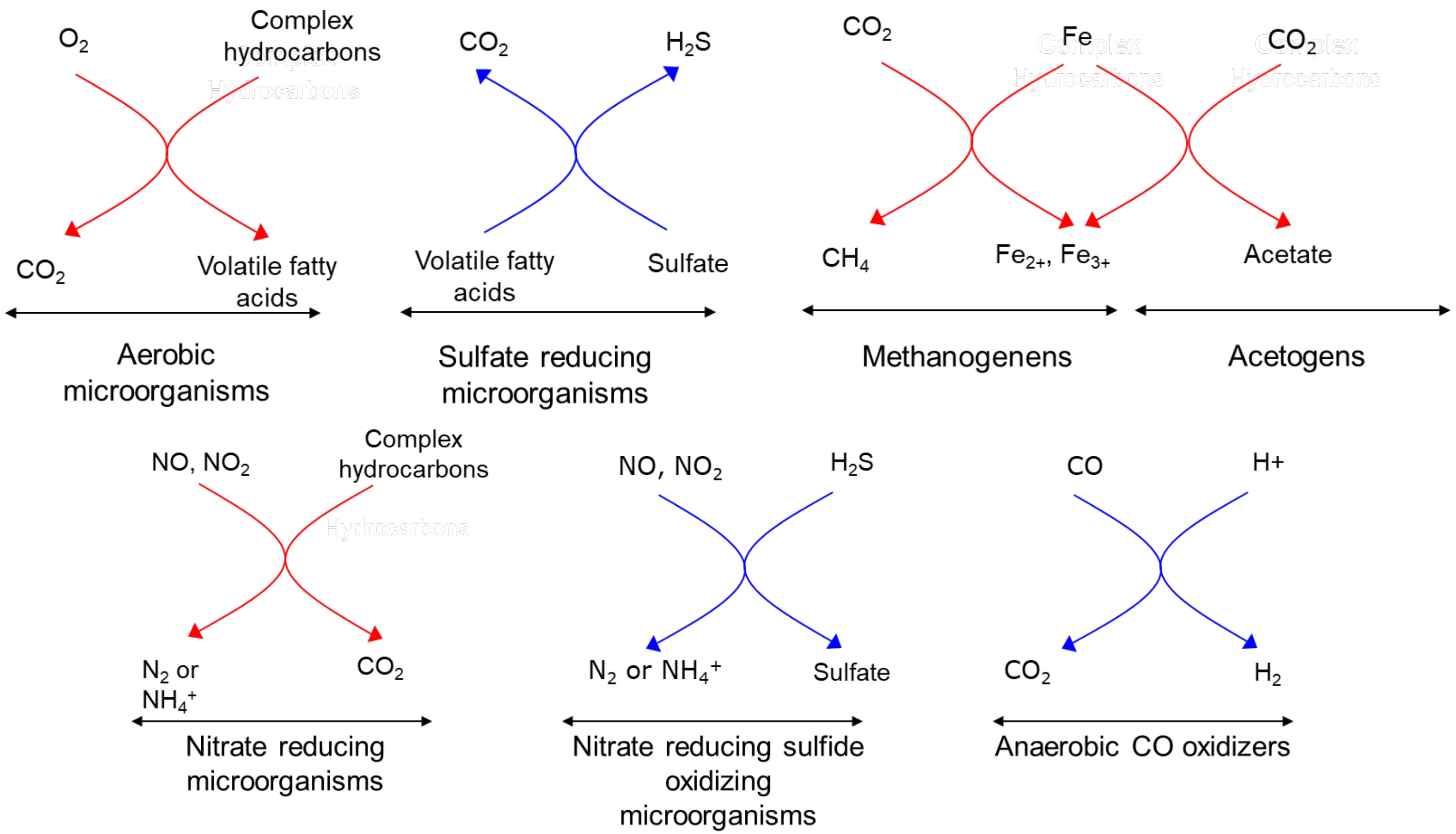


Electron donor: Acetate (C from 0 → +4)

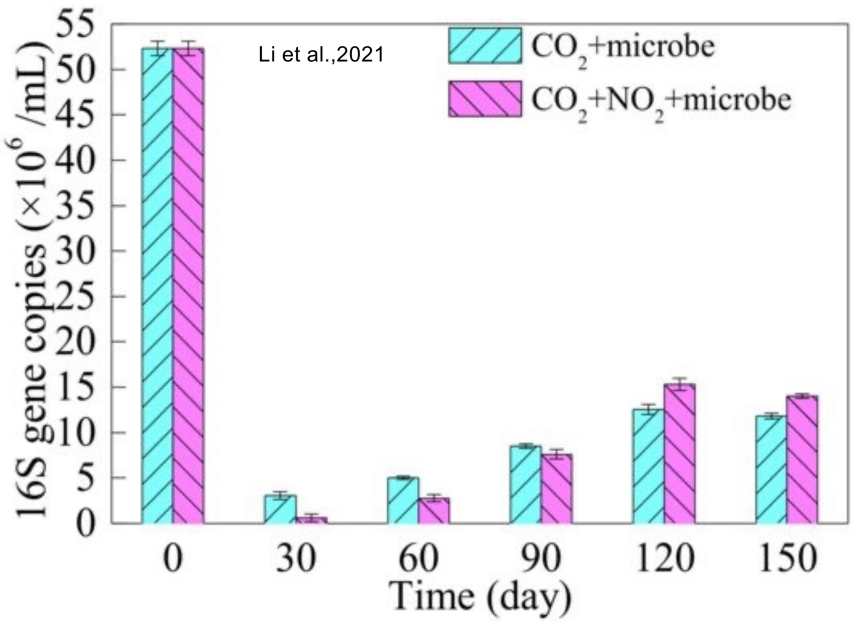
Electron Acceptor: Sulfate (S from +6 to → -2)

Biochemical effects

Biologic reactions fuelled by CO_2 injection



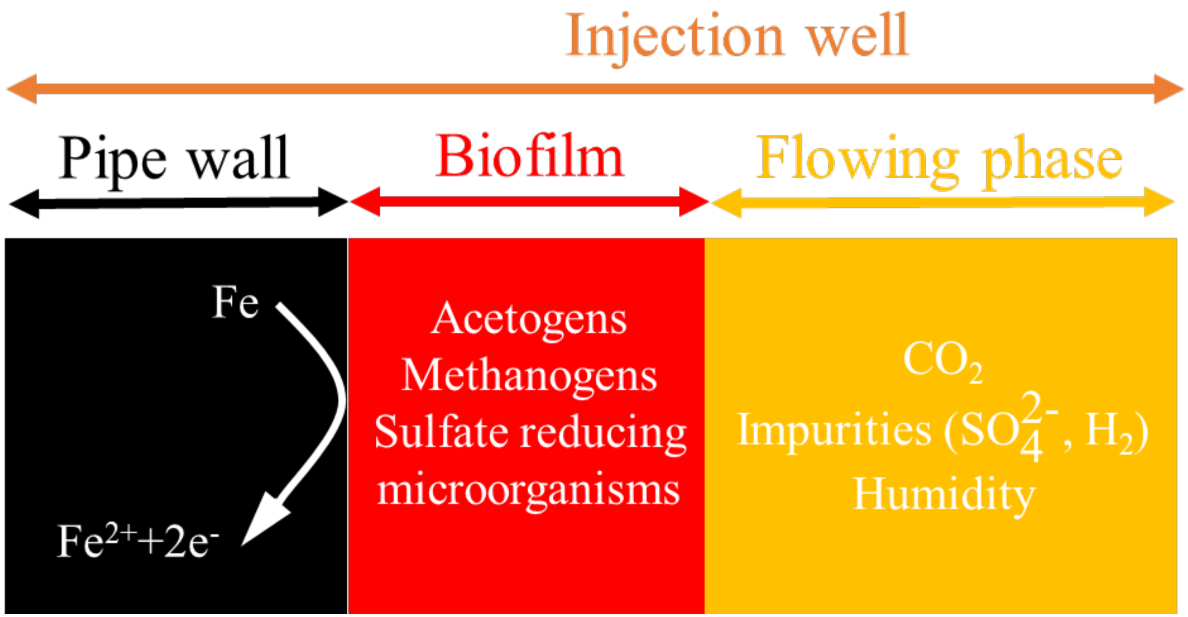
Biochemical effects



- Microbial activity can be sustained over decades to centuries due to the presence of all elements required for microbial growth.
- CO_2 dissolution of reservoir rock can release sulfate, phosphate minerals, etc that can be utilized by microorganisms. The resulting metabolic products can interact with the formation brine and produce precipitates, and together with the produced biomass, they can influence porosity, permeability and consequently fluid flow behavior.

- Impurities in the CO2 stream impact pH and the extent of microbial activity
- The increase in the microbial activity affects porosity, permeability and corrosion

Biochemical effects



Conclusions

- Extensive research exists on the development of EoS for CO_2 with impurities
- The reduction in the storage capacity is the main consequence of the physical effects of impurities in the CO_2 stream
- Modelling studies on sandstones show that impurities have a minor effect on the porosity and permeability
- Geochemical reactions triggered by the presence of impurities are expected to play a greater role in carbonates
- Limited experimental data on the effect of impurities in carbonates
- Impurities cause and intensify biological processes that affect injectivity, storage, and containment (well integrity, caprock sealing)