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# Impact of pH on hydrogen oxidizing redox processes in aquifers due to gas intrusions

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## Geo Energy Storage

- Aim of at least 80% renewable power production by 2050 in Germany
- Fluctuations in renewable energies can be met by energy storage solutions
- ANGUS+ investigates several issues concerning geological energy storage
  - Gas or heat storage
  - Parameterization, modeling, monitoring workflow
  - Studies on geochemical reactions, multiphase reactive flow and transport, geophysical exploration and monitoring, space planning, etc.

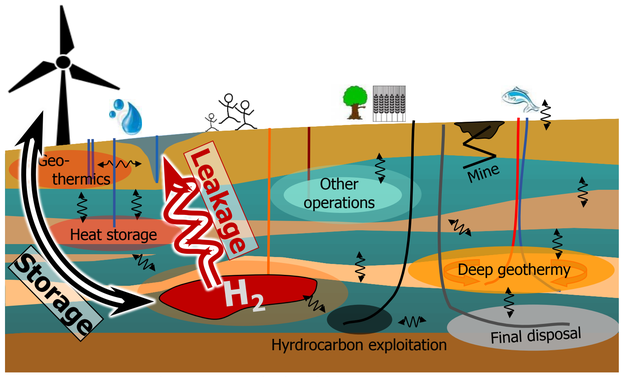
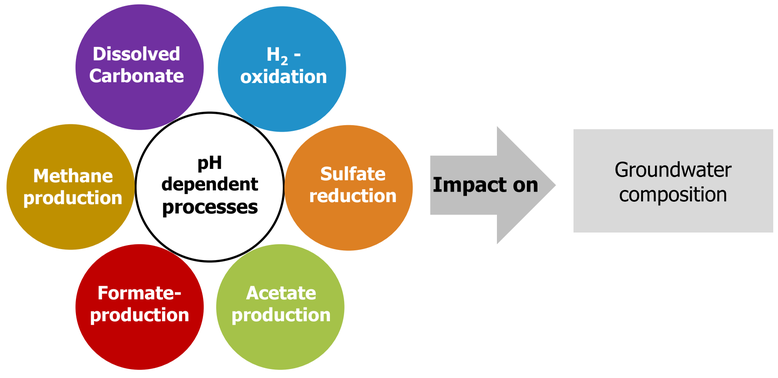



*Figure 1. Options and interactions of subsurface energy storage.*

- Investigating the effects of gas leakages into aquifers as a part of ANGUS+:
  - Shallow groundwater: often specially protected and used as drinking water
  - Experimental investigation on the effects of air, $H_2$, and $CH_4$ leakages
    - Identification of important hydrogeochemical redox reactions
    - Parameterization: reaction kinetics, equilibrium, lag phases, etc.
  - Development of reaction models as bases for virtual scenario models
    - Potential risks for groundwater, time frames, monitoring targets, etc.

## Concept of Investigation and Aims

Laboratory experiments using natural aquifer materials support the development of reaction models describing the effects of hydrogen gas pressures up to 15 bars




## Experimental Setup

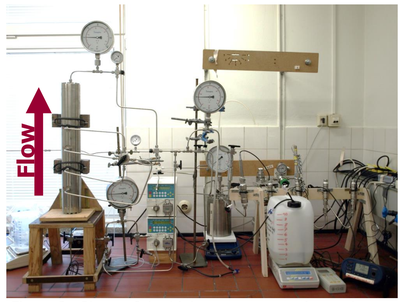



*Figure 2. Photo of the high pressure experimental apparatus.*

- Gas mixture and partial pressure are the main variables
  - 100% $H_2$
  - 99% $H_2$ + 1% $CO_2$ to reduce pH
  - p($H_2$): 2 - 15 bars ($H_2$ in 0 - 150 m depth)
- Column: Ø = 4 cm, L = 50 cm
- Flow speed: ~2 m/day
- Run time: 1.5 years
- Groundwater and sediment with microorganisms were taken from a shallow Pleistocene aquifer
- Analytics: pH, anions (IC), cations (ICP-AES), TIC-TOC, dissolved gases (GC)

## Hydrogen-Coupled Redox Reactions

- All investigated processes are independent from p($H_2$)
- Increase of one pH level during column percolation
- $H_2$ oxidation and $SO_4^{2-}$ reduction
  - $0^{th}$ order rates at pH 8 to 10 (644 to 89 µM/h and 51 to 12 µM/h)
  - at pH 7 to 8 faster rates near column's inflow
- Acetogenesis and formate production
  - At pH 8 to 10 acetogenesis dominates
  - At pH 7 to 8 acetogenesis shows a linear trend (3 to 5 µM/h) or is not observed and formate production starts ($0^{th}$ order rates of 38 to 364 µM/h)
- Methanogenesis as a minor process below pH 8

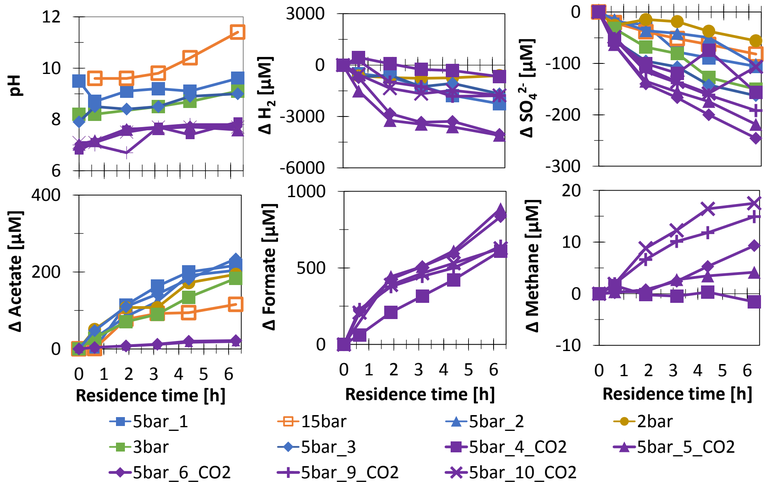



*Figure 3. Concentration profiles of pH, hydrogen, sulfate, acetate, formate and methane. Concentrations for all parameters except pH are calculated as delta to the respective inflow concentration. Gas pressure used in each experiment is indicated by the initial number in legend entries (X bar), second number indicates chronological order of profile (5 bar_X) and "$CO_2$" indicates the use of $H_2$-$CO_2$ gas mixture to reduce pH.*

## Impact of pH

- Sulfate reduction increases with decreasing pH
- Organic substances:
  - pH range for acetogenesis between pH 7 and 10, optimum at pH 8.5
  - Formate and methane production starts at pH values lower than 7.5
  - Increase of acetate, formate and methane production (equal to TOC production in the experiments) with decreasing pH
- Change of two parameters: Using $CO_2$ pH was lowered **and** TIC concentration increased
- Increasing microbial activity: pH dependency vs. slow development of cell numbers

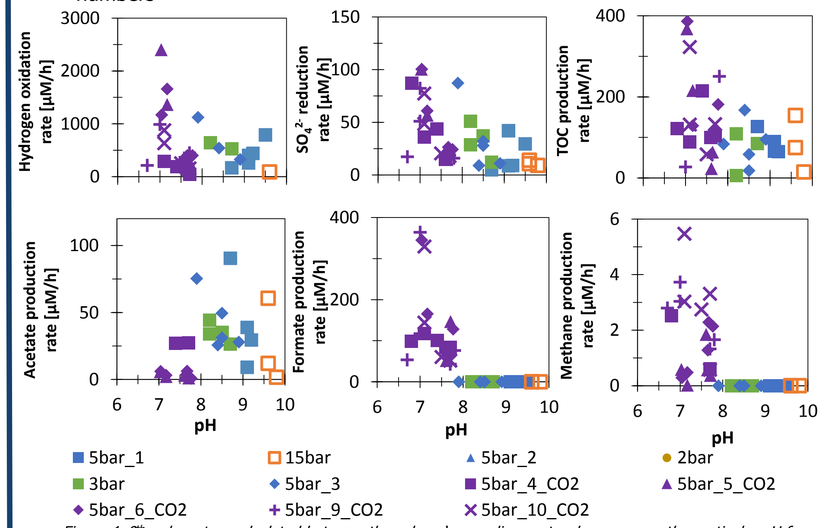



*Figure 4. $0^{th}$ order rates, calculated between the column's sampling ports, shown versus the particular pH for processes of hydrogen oxidation, sulfate reduction, formate production and acetogenesis. Gas pressure used in each experiment is indicated by the initial number in legend entries (X bar), second number indicates chronological order of profile (5 bar_X) and "$CO_2$" indicates the use of $H_2$-$CO_2$ gas mixture to reduce pH.*

## Conclusion

**Impact of pH on $H_2$ oxidizing redox processes**

- **Increasing sulfate reduction with decreasing pH**
- **Maximum acetogenesis at pH 8.5**
- **Formate and methane production below pH 7.5**
- **General increase of TOC production with decreasing pH**

**Consider pH as important factor for groundwater composition at a specific storage site**

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