# Abiotic mineral-fluid-gas reactivity in underground $H_2$ storage: A kinetic rate law for reductive pyrite dissolution from 60-150 °C and up to 150 bar $P_{H2}$

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Equation (1):   $$R = Ae^{-E_a/RT}(a_{H^+})^{-n}\left(P_{H_2}\right)^m\left(1-\frac{Q}{K}\right)$$
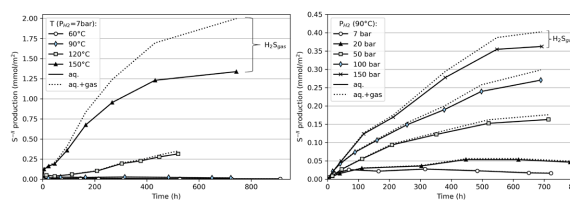


Fig. 1: Normalized sulfide production (mmol/m²) as a function of time, temperature (left) and $P_{H2}$ (right). Aqueous sulfide concentrations were measured by methylene blue spectrophotometry while gaseous $H_2S$ was computed in equilibrium.

Hydrogen is an energy storage medium as excess energy from renewable sources can be used to produce green $H_2$. Large-scale $H_2$ storage in subsurface environments (e.g. salt caverns, depleted gas fields, aquifers) can support the energy transition. However, fluid-rock-$H_2$ interactions are a concern as $H_2$ is a potent electron donor. For example, the reductive dissolution of pyrite produces gaseous $H_2S$, a toxic and corrosive contaminant of the stored $H_2$ gas [1, 2].

To study the kinetics of reductive pyrite dissolution at conditions relevant to underground $H_2$ storage, anoxic alteration experiments of pyrite ($\phi$ = 50-100 μm) were conducted at $T$ = 60-150 °C, $P_{H2}$ = 7-150 bar and $pH$ ~ 3.8-8.6 in 30 mmol/L NaCl solutions. Experiments were carried out in $H_2$-pressurized batch reactors made either of titanium or coated stainless steel. The temporal evolution of dissolved sulfide concentrations was measured by methylene blue spectrophotometry (Fig. 1). Electron microscopy of post-mortem pyrite grains revealed the formation of authigenic pyrrhotite and magnetite. The derived kinetic rate law was based on total (aqueous + gas) sulfide production rates determined at 12h, which represents far-from-equilibrium conditions. For implementation in geochemical codes, the rate law was based on the general form given in Eq. (1).

Reductive pyrite dissolution was upscaled over a 30-year period using batch models to simulate $H_2$ storage into a sandstone depleted gas field, containing 0.13 vol.% pyrite, 4.6 vol.% carbonates at 117 °C and an injection pressure of 150 bar (PHREEQC, modified Thermoddem database [3]). The models predicted buffered gas concentrations of 28 ppm $H_2S$ and 4.4 % $CO_2$. In a sensitivity study, calculated gas concentrations varied on the order of $10^0$-$10^3$ ppm $H_2S$, emphasizing the role of Fe-bearing minerals (e.g., chlorite, siderite) as a source of $Fe^{2+}_{(aq)}$ for scavenging dissolved sulfide ions.

References:

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