

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

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Hydrogen production from excess energy and its storage can help increasing the efficiency of solar and wind in the energy mix. Therefore, hydrogen needs large-scale intermediate storage independent of the intended later use as hydrogen gas or as reactant to produce methane in the Sabatier process. A possible storage solution is using the geological subsurface such as caverns built in salt deposits or aquifers that are not used for drinking water production. However, underground storage of hydrogen gas potentially leads to accidental gas leakages into near-surface potable aquifers triggering subsequent geochemical processes. These leakages pose potential risks that are currently not sufficiently understood.

To close this gap in knowledge, a high-pressure laboratory column system was used to simulate a hydrogen gas intrusion into a shallow aquifer. Water and sediment were gained from a sandy Pleistocene aquifer near Neumünster, Germany. In the first stage of the experiment, 100% hydrogen gas was used to simulate dissolved hydrogen concentrations between 800 and 4000 μM by varying $p\text{H}_2$ between 2 and 15 bars. pH values rose to between 7.9 and 10.4, partly due to stripping CO_2 from the groundwater used during H_2 gas addition. In a second stage, the pH was regulated in a range of 6.7 to 7.9 by using a gas mixture of 99% H_2 and 1% CO_2 at 5 bars of total gas pressure.

Observed processes included hydrogen oxidation, sulfate reduction, acetogenesis, formate production, and methanogenesis, which were independent of the hydrogen concentration. Hydrogen oxidation and sulfate reduction showed zeroth order reaction rates and rate constants (106 to 412 $\mu\text{M}/\text{h}$ and 12 to 33 $\mu\text{M}/\text{h}$, respectively) in the pH range between 8 and 10. At pH levels between 7 and 8, both reactions started out faster near the column's inflow but then seemed limited towards the column's outflow, suggesting the dependence of sulfate reduction on the pH-value. Acetogenesis dominated the pH range between 8 and 10 (first order rate constants between 0.029 and 0.036 1/h). Between pH 7 and 8, acetogenesis showed a linear trend (zeroth order rates between 3 and 5 $\mu\text{M}/\text{h}$) whereas formate production became the main process (zeroth order rates between 38 to 197 $\mu\text{M}/\text{h}$) together with methanogenesis as a minor process.

The results indicated a strong dependency of the biogeochemical hydrogenotrophic redox reactions on the pH milieu. Thus, pH buffers such as dissolved or solid phase carbonates should be taken into account when predicting effects a hydrogen leakage may have on shallow aquifers. Additionally, parameters derived from the observed processes and their rates allow the design of a process based numerical model simulating a hydrogen intrusion into a shallow aquifer. Consequently the presented outcomes allow an exemplary quantification of the resulting geochemical effects.

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