

## **Geochemical effects of compressed air, methane, or hydrogen intrusion into shallow aquifers**

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The fluctuating energy yield of renewable sources, most importantly wind and solar, implies the emerging necessity of energy storage. Already operating possibilities for geological energy storage include storage of compressed air (CAES), methane, and hydrogen. For the safe and sustainable implementation of subsurface energy storage, site specific risk assessment studies and elaborated monitoring strategies are needed, based on proper process understanding. In case of gas storage, this process understanding must include gas-specific reactions to be expected in shallow aquifers following a leakage of compressed air, methane, or hydrogen, and therefore potentially changing the composition of the groundwater, which is protected by law.

As the geochemical reactions potentially following gas leakages were not known in a sufficient extent, experiments representing relevant hydrogeological conditions were carried out. The experimental approach included batch and column experiments using mainly sediment from a shallow Pleistocene aquifer percolated by the groundwater from the same aquifer. This water was saturated with the respective gas to simulate a leakage environment in a shallow aquifer.

Leakage of compressed air resulted in pyrite oxidation (rates up to 4  $\mu\text{M}/\text{h}$ ). In our experimental conditions with oxygen partial pressures between 0 and 11 bars pyrite oxidation caused minor (up to 0.5 mM) increase in sulfate concentration and minor (up to 0.5) decrease in pH. The transfer function on reaction kinetics developed using PHREEQC based on the experimental reaction rates for upscaling the results includes a passivation inhibiting more than 90% of the pyrite reactivity.

Methane oxidation coupled to reduction of nitrate, and especially sulfate is known from various groundwater and marine environments. However, fugitive methane does not cause detectable changes in groundwater within one year in our experiments. This acknowledges earlier field studies describing no methane oxidation if methane or its electron acceptors are newly introduced into an aquifer, even if they are usually not simultaneously present in natural conditions.

In contrast, elevated (in the mM range instead of the natural nM range) concentration of hydrogen triggers a series of redox reactions. Changes in groundwater composition were found in experimental groundwater-aquifer conditions created by batch, reactor and column experiments involving hydrogen partial pressures between 1 and 25 bars. The resulting reduction of ferric iron, nitrate (rates up to 10.4  $\mu\text{M}/\text{cubic cm sediment}/\text{h}$ ), sulfate (rates up to 42 nM/cubic cm sediment/h), and carbonate have major effects on groundwater, including the increase of acetate (rates up to 85 nM/cubic cm sediment/h), nitrite, and sulfide concentrations and pH (by up to 1.5); along with decreasing (by ca. 100  $\mu\text{S}/\text{cm}$ ) electrical conductivity.

These experimental conclusions have direct applications beyond the description of conditions not explicitly studied before. The observed hydrogeochemical behavior of gas-saturated hydrogeochemical environments improves process understanding for gas leakage scenarios and serves as base for future planning and characterization of gas storage sites as well as leakage monitoring strategies.