

CO₂ induced mineralogical and geochemical changes in a storage system - comprehensive CO₂-exposure experiments on reservoir and cap rock samples and mineral separates

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In order to understand the geochemical behavior of reservoir systems we study CO₂-brine-rock as well as CO₂-brine-mineral interaction during comprehensive laboratory experiments at P-T conditions typical for geological CO₂ storage scenarios. In a first approach, we performed static, long-term experiments on reservoir rocks recovered from ~630 m depth at the Ketzin pilot CO₂ storage site, Germany. These were exposed to pure CO₂ and synthetic reservoir brine at 5.5 MPa and 40 °C. Autoclaves were opened and sample aliquots taken after 15, 21, 24 and 40 months, respectively.

For a second set of static experiments, we used core samples of silty, cap-rock-like rocks from 625 m depth directly overlaying the above mentioned sandstones. Three core samples were exposed to pure CO₂ and synthetic reservoir brine at 7.5 MPa and 40 °C. Samples were taken after two, four and six months, respectively. Parallel, one autoclave was filled with N₂ (instead of CO₂) and also reacted for 6 months. This set of experiments is completed and organic and inorganic fluid data, XRD, SEM as well as EMP data available for interpretation.

In a third approach, we perform monomineralic experiments using a new hydrothermal rocking autoclave system equipped with flexible titanium cells allowing for isobaric/isothermal sampling. Each mineral is separately exposed to pure CO₂ and 2 M NaCl brine at 20 MPa and 80 °C. Siderite, illite and labradorite are scheduled to react for one, two and three weeks, respectively. For each experiment, at least six fluid samples are taken. A first set of experiments is completed and repeat runs for each specimen are currently ongoing.

Long-term experiments on reservoir sandstone revealed minor mineralogical changes. XRD data showed decreasing proportions of analcime, chlorite, hematite and illite, and increasing proportions of quartz. Corrosion textures were observed for plagioclase, K-feldspar and anhydrite. The chemical composition of plagioclase indicated a change from intermediate to Na-rich and albite endmember compositions. While Na⁺, Mg²⁺ and Cl⁻ increased slightly, K⁺, Ca²⁺ and SO₄²⁻ increased significantly during the runs. Petrophysical data show tendentially increasing porosities and permeabilities for the majority of samples during the experiments. Reactive geochemical modeling using PHREEQC code was performed to reproduce experimental observations. Assuming thermodynamic equilibrium, preliminary reactive geochemical modeling of the observed CO₂-fluid-sandstone interactions showed that the measured evolution of fluid composition is consistent with precipitation of albite and dissolution of anhydrite and illite, respectively.

Due to the highly heterogeneous character of the Stuttgart Formation that formed in a fluvial environment it is often difficult to distinguish between natural, lithostratigraphic variability and CO₂-related changes. The mineralogical and geochemical measurements imply dissolution and albitization of plagioclase next to dissolution of K-feldspar and anhydrite. The chemical integrity of the Ketzin reservoir is not significantly affected by CO₂.

After analysis and interpretation of data from the other two sets of experiments (on cap-rock-like samples and monomineralic specimens) and completed reactive geochemical modeling, a much more comprehensive and general statement on the geochemical behavior of reservoir systems with regard to injected CO₂ will be at hand.