



Investigation of pore size related parameters during long-term CO₂-brine-rock interaction from batch experiments and from in situ rock cores after 4 years of geological CO₂ storage at the Ketzin pilot site (Germany)

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The objective of this study is to investigate long-term effects of injected CO₂ on pore size related parameters. Changes in porosity, pore geometry and distribution, effective permeability, and capillary entry conditions influence the development of static and dynamic storage capacity and injectivity.

For the batch experiments core samples from the target reservoir horizon and its directly overlying cap-rock of the Triassic Stuttgart Formation at the Ketzin pilot storage site in Germany drilled in 2007 (observation well Ktzi 202) were exposed to pure CO₂ and synthetic reservoir brine in corrosion-resistant, high-pressure autoclaves under in situ P-T conditions over various time periods.

For the first run with reservoir sandstone, seven inner core section (Ø 50 mm x 100 mm) and additional rock fragments were stored in separate autoclaves for 40 months. After 15, 21, 24, and 40 months, respectively, all autoclaves were opened and samples were taken for mineralogical, geochemical, microbiological and petrophysical investigations. In a second run, three parallel siltstone samples were placed in autoclaves and exposed to CO₂ and synthetic reservoir brine with run durations of 2, 4 and 6 months; a fourth cap-rock sample was exposed to N₂ for 6 months and served as blind-run.

The samples were investigated by NMR relaxation and mercury injection porosimetry (MIP). The NMR amplitude is related to fluid filled porosity. In addition, the distribution of NMR-T₂ values reflects the pore sizes. The porosity of the connected pore system and the distribution of pore throats can be derived from the MIP. Based on the data, empirical models were used to estimate corresponding permeabilities as well as displacement, threshold, and critical pore pressure from the mercury data.

The porosity data of the batch experiments determined by NMR and MIP are comparable and consistent with the logging data. The data of the reservoir experiments indicate only small changes of the pore size related properties. The distinguishment between natural, lithostratigraphic variability and experimentally induced, CO₂ related changes is difficult. The second dataset of parallel siltstone samples show also only very small changes in values over time and no effect at the N₂ experiment.

In 2012, after injection of 61 000 tons CO₂, an additional well (Ktzi 203) was drilled and new rock cores were recovered in October 2012. In total 100 core samples from the overlaying caprock and the reservoir horizon with traceable CO₂ were investigated by NMR relaxation. Samples from inner and outer parts of the drill core were used in order to separate the influence of potash drilling fluid. The NMR data and derived rock properties are comparable to the pre-injection values determined for the older wells. Due to the heterogeneous character of the Stuttgart Formation it is difficult to estimate definite CO₂ induced changes from petrophysical measurements.

Based on present data, the changes in pore size related properties of the siliciclastic rocks of the Ketzin reservoir and cap-rock are only minor. These pore size related parameters are not significantly affected by pure CO₂ with only marginal influence on reservoir capacity and injectivity. The integrity of the reservoir formation at Ketzin is not affected.