



Flow and reaction along the cement-rock interface during CO₂ injection. Laboratory experiments and modeling.

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The interface between reservoir/cap rocks and the Portland cement around boreholes is a possible leakage pathway during deep geological injection of CO₂. To study the alteration of cement and rock, laboratory experiments involving flow along this interface were performed. Cylindrical cores of about 5 cm in length and 2.5 cm in diameter and composed of half-cylinders of cement and rock (sandstone, limestone, marl) were used. They were reacted with a synthetic sulfate-rich saline groundwater under (a) atmospheric conditions (10^{-3.4} bar CO₂, 25°C, pH 6.2) and (b) supercritical conditions (130 bar CO₂, 60°C, pH about 3) in flow-through reactors. Tracer (LiBr) tests were performed prior to the injection of the saline solution in the atmospheric experiments to characterize cement diffusivity. The evolution of solution chemistry at the outlet was monitored over time. Rock and cement were analyzed at the end of the experiments (SEM, XRD, profilometry).

In the atmospheric experiments pH increased up to about 11 (tracer tests) and 8 (groundwater injection, brucite precipitation). Calculated outlet pH was about 4 under supercritical conditions. Major-element concentrations showed little change during the atmospheric experiments, while Ca excess and S deficit were observed under supercritical conditions. Intense brucite precipitation was observed on the cement surface after the atmospheric experiments, while an apparently amorphous red-colored phase precipitated under supercritical conditions. Rock surfaces evidenced calcite dissolution in the supercritical experiments, while alteration was little in the atmospheric experiments. Some gypsum precipitation was also observed. Interface aperture increased during the supercritical experiments.

2D reactive transport modeling (CrunchFlow) was used to interpret the results. Phase reactivities (surface areas), and in some cases diffusion coefficients (rock and cement), were adjusted to fit models to measurements (solution and solid). Under atmospheric conditions, brucite precipitation (and decrease in porosity) results from the mixing by diffusion of the Mg in the input solution and the alkalinity in the cement. Ca from portlandite dissolution and sulfate from the input solution drives the precipitation of gypsum. For the supercritical experiments, model results show intense dissolution of portlandite, ettringite, siliceous hydrogarnet and hydrotalcite, extending for about 3 mm into the cement and causing an increase in porosity. The Ca released precipitates as calcite, with carbonate provided by the CO₂-rich input solution. As the portlandite front moves into the cement, calcite dissolves next to the interface and some of the Ca precipitates as gypsum. Coupled calcite dissolution and gypsum precipitation also occurs, to a lesser extent, in the rock side. The calculations also result in the precipitation of small amounts of ferrihydrite, gibbsite and boehmite, which could correspond to the observed red-colored precipitates. Importantly, the adjusted values of the reactive surface areas for the different experiments point to a larger reactivity of the cement under supercritical conditions.

