CO$_2$-brine-mineral Reactions in Geological Carbon Storage: Results from an EOR Experiment

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Dissolution of CO$_2$ in brines and reactions of the acid brines ultimately dissolving silicate minerals and precipitating carbonate minerals are the prime long-term mechanisms for stabilising the light supercritical CO$_2$ in geological carbon storage. However the rates of dissolution are very uncertain as they are likely to depend on the heterogeneity of the flow of CO$_2$, the possibility of convective instability of the denser CO$_2$-saturated brines and on fluid-mineral reactions which buffer brine acidity. We report the results of sampling brines and gases during a phase of CO$_2$ injection for enhanced oil recovery in a small oil field. Brines and gases were sampled at production wells daily for 3 months after initiation of CO$_2$ injection and again for two weeks after 5 months. Noble gas isotopic spikes were detected at producing wells within days of initial CO$_2$ injection but signals continued for weeks, and at some producers for the duration of the sampling period, attesting to the complexity of gas-species pathways.

Interpretations are complicated by the previous history of the oil field and re-injection of produced water prior to injection of CO$_2$. However water sampled from some producing wells during the phase of CO$_2$ injection showed monotonic increases in alkalinity and in concentrations of major cations to levels in excess of those in the injected water. The marked increase in Na, and smaller increases in Ca, Mg, Si, K and Sr are interpreted primarily to result from silicate dissolution as the lack of increase in S and Cl concentrations preclude additions of more saline waters. Early calcite dissolution was followed by re-precipitation. $^{87}$Sr/$^{86}$Sr ratios in the waters apparently exceed the $^{87}$Sr/$^{86}$Sr ratios of acetic and hydrochloric acid leaches of carbonate fractions of the reservoir rocks and the silicate residues from the leaching. This may indicate incongruent dissolution of Sr or larger scale isotopic heterogeneity of the reservoir. This is being investigated further by analyses of rock and mineral clasts from core.

A surprising result of this study is the extent to which CO$_2$ has dissolved in brines to drive fluid-rock reactions during the short duration of this experiment. However, simple one-dimensional flow modelling with lateral diffusion of CO$_2$ into brines demonstrates that the natural heterogeneities in permeability in the reservoir on the scale of ~1 m are sufficient to cause extensive fingering of the CO$_2$ along the highest permeability horizons. Because flow of brines is fastest in the relatively high permeability layers adjacent to the CO$_2$-bearing layers, production of this more CO$_2$-rich water dominates the output from production wells.