Modeling CO_2–H_2S–Water–Rock Interactions at Williston Basin Reservoir Conditions

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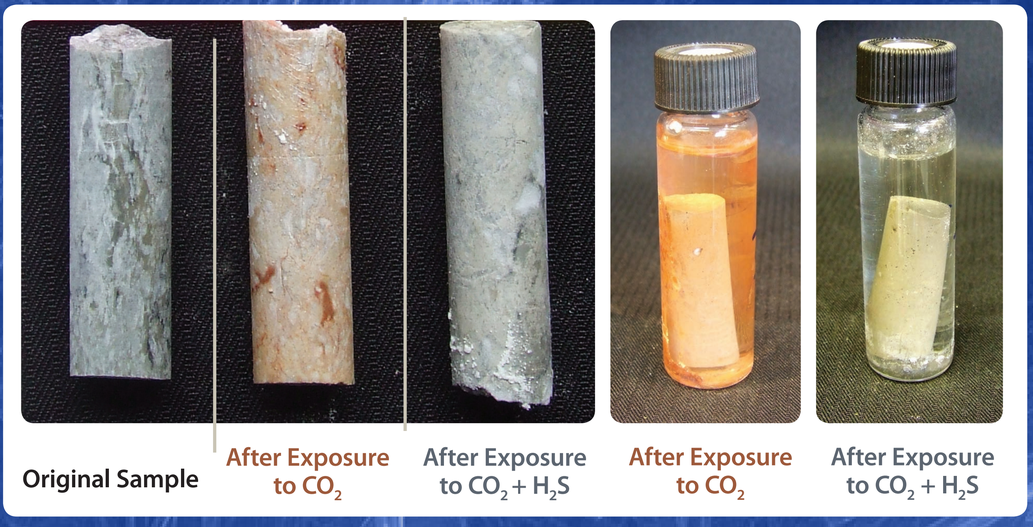
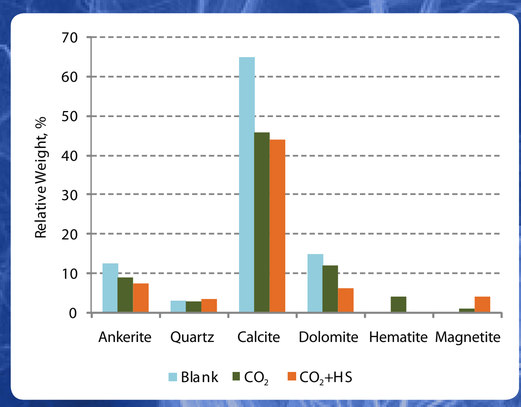
Abstract

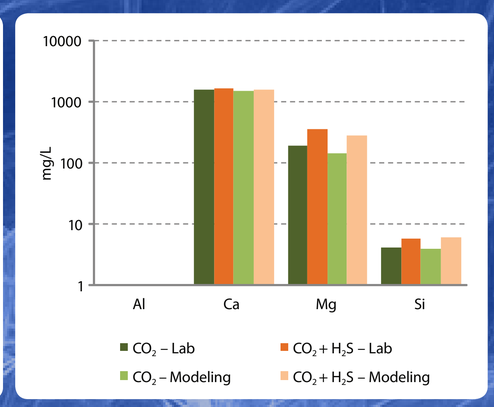
A series of laboratory experiments, field observations, and numerical modeling of geochemical reactions have been conducted to determine the chemical kinetics of potential mineral dissolution and/or precipitation caused by the injection of carbon dioxide (CO_2) and sour gas. Kinetic experiments were conducted using core samples from potential Williston Basin storage formations and pure mineral samples (e.g., calcite, dolomite, siderite, etc.) obtained from vendors. Samples were analyzed using x-ray diffraction (XRD) and QEMSCAN® techniques. Two sample sets consisting of 16 samples each, under the same experimental conditions, were "soaked" for a period of 4 weeks at 2500 psi (172 bar) and 176°F (80°C) in synthetically generated brine. Over that time period, one set was exposed to pure carbon dioxide and the other to a mixture of CO_2 (88 mol%) and H_2S (12 mol%). The initial XRD mineralogical analysis of selected samples indicates the presence of the following minerals: anhydrite, calcite, dolomite, forsterite, halite, illite, magnetite, and quartz. The main objectives of this work were 1) to determine possible mineral reactions of the Madison Group, Broom Creek Formations, and Tyler Formations of Williston Basin, North Dakota with CO_2 and sour gas; 2) to identify potential operational concerns; 3) to compare differences in mineral reactions between pure CO_2 and sour gas injection scenarios; and 4) to adjust kinetic reaction rates for geochemical modeling tools with experimental observations. This work was performed by the Energy & Environmental Research Center through the Plains CO_2 Reduction Partnership, one of the U.S. Department of Energy National Energy Technology Laboratory's Regional Carbon Sequestration Partnerships.

Results

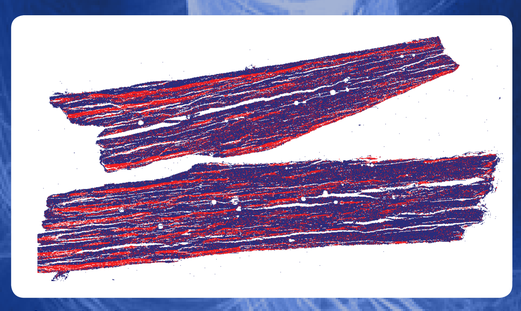


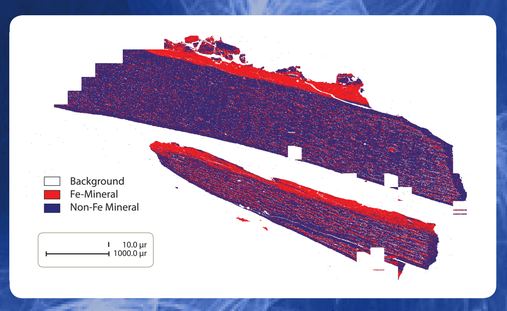
Mississippian Mission Canyon Limestone sample collected from a depth of 8140 ft (2481 m) saturated with brine (NaCl, 10 %) and exposed to pure supercritical CO_2 and a mixture of supercritical CO_2 (88 mol%) and H_2S (12 mol%) under a pressure of 2100 psi (145.4 bar) and temperature of 176°F (80° C). The left side of the figure represents vacuum-dried-after-exposure samples compared with the original specimen; and the right side illustrates samples saturated in fluid after experiment completion.



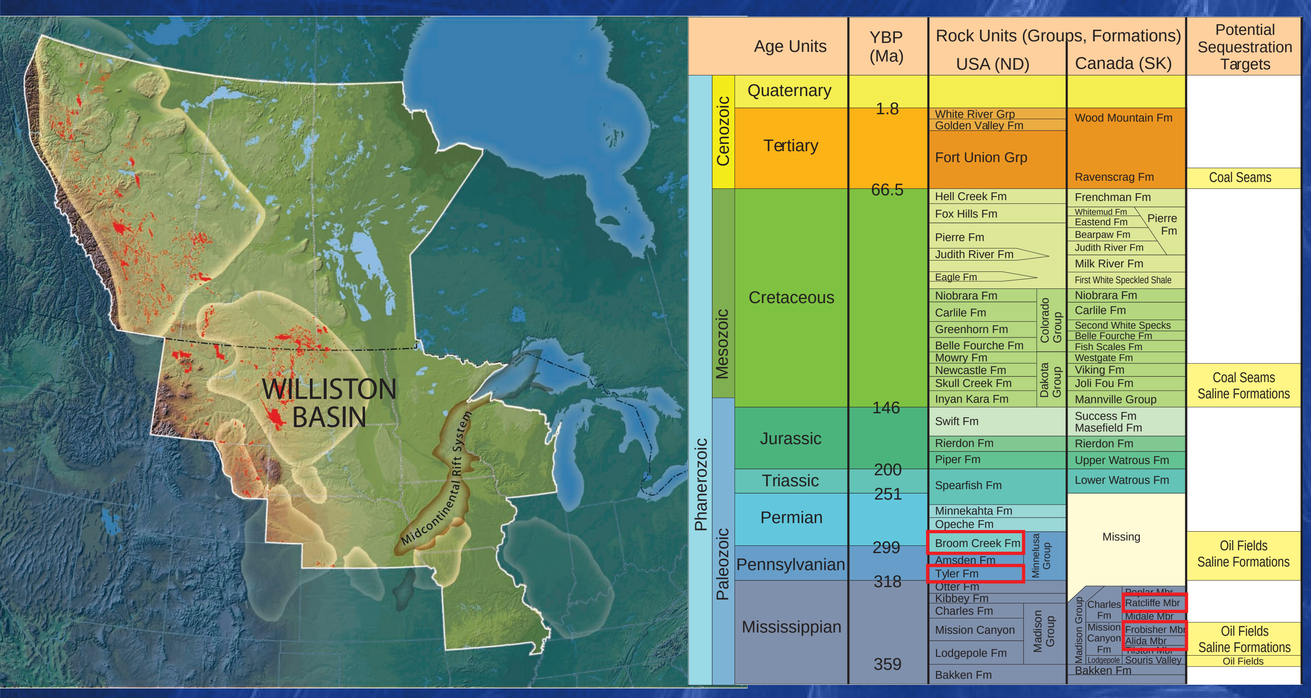


On the left: The combined mineralogical analysis of initial (unexposed) sample (blue color), sample exposed to CO_2 (dark green), and sample exposed to CO_2 and H_2S (orange). On the right: The exposed water composition analysis for metals compared to numerical modeling.





The refined QEMSCAN image of the Broom Creek Formation rock, which illustrates the spatial distribution of iron content within the sample. On the left: unreacted sample. On the right: sample after exposure to CO_2.



Rock Unit Selection

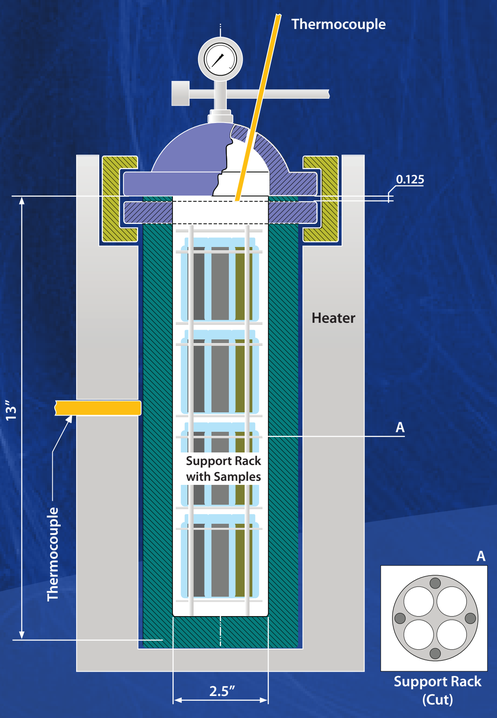
To evaluate potential chemical and physical reactions between CO_2 and selected Williston Basin rock units, samples representing three different formations were tested in bench-scale laboratory experiments. Numerical modeling of geochemical reactions was performed and verified with laboratory results. The samples were chosen as a part of the Williston Basin characterization effort, based on both availability and on the likelihood of future exposure to injected CO_2. In previous work, five different formations were subjected to initial evaluation, and powdered rocks were used in order to obtain initial results. A further, more focused investigation of three different formations was undertaken: Madison Group (limestone- and dolostone- dominated samples), Broom Creek (dolomite and calcite cemented sandstone), and Pennsylvanian–Tyler Formation (sandstone with carbonates and clays). All Williston Basin samples were obtained through the North Dakota Geological Survey's Core Library, located on the campus of the University of North Dakota.

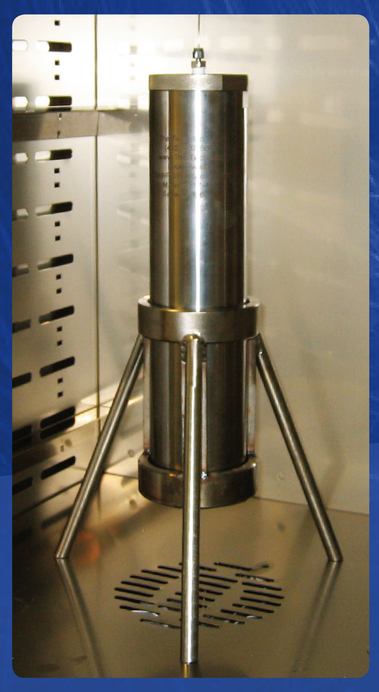
Summary

This preliminary geochemical assessment Madison Group, Broom Creek Formations, and Tyler Formations of Williston Basin indicated that there are no immediate operational concerns for both cases of injection scenarios (pure CO_2 and sour gas). The analysis of obtained reaction products suggests that 1) there is no strong evidence for higher degradation of samples exposed to a mixture of CO_2 and H_2S if compared to the pure CO_2 stream; however, 2) carbonate rocks seem to be more unstable if exposed to the acid gas if compared to pure CO_2 3) if H_2S is present in the stream, it seems to be more dominant in the reactions; and 4) reactivity of the sample is strongly driven by its mineralogy.

The mineralogical analysis performed with various analytical tools (x-ray fluoresence, XRD, and QEMSCAN) required verification with numerical modeling tools. Often, the error in instrument tolerance, small-scale sample heterogeneity, or measurement error can be corrected by thermodynamic modeling suggestions.

Experimental Setup and Conditions





CO_2 Partial Pressure	2250 psi/155 bar
Temperature	158°F/70°C
Gas Mixture	1) CO_2 – 100 mol% 2) CO_2 – 67.3 mol% H_2S – 32.7 mol%
Mass of Sample	10–15 g
Type of Sample	Core plugs
Saturation Conditions	Synthetic brine NaCl, 10% by weight
Time of Exposure	4 weeks

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