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

Yevhen I. Holubnyak[1], Steven B. Hawthorne, Blaise A.F. Mibeck, David J. Miller, Jordan M. Bremer, James A. Sorensen, Edward N. Steadman, John A. Harju

University of North Dakota Energy & Environmental Research Center, 15 North 23rd Street, Stop 9018, Grand Forks, ND 58202-9018, USA

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Abstract

A series of laboratory experiments, field observations from a small-scale CO_2 enhanced oil recovery project, 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 CO_2 and of sour gas. Kinetic experiments were conducted using core samples from potential Williston Basin storage formations. Two sample sets consisting of 16 samples each, under the same experimental conditions, were "soaked" for a period of 4 weeks at 172 bar and 80°C in synthetically generated brine conditions. Over that time period, one set was exposed to pure carbon dioxide and the other to a mixture of carbon dioxide (88 mol%) and hydrogen sulfide (12 mol%). The analysis of obtained reaction products suggests that 1) there is no strong evidence for higher reactivity of samples exposed to a mixture of CO_2 and H_2S if compared to the pure CO_2 stream; however, 2) if H_2S is present in the stream, it seems to be more dominant in the reactions; and 3) reactivity of the sample is strongly driven by its mineralogy.

Keywords: CO_2 storage; geochemical modeling; batch laboratory experiments; acid gas storage

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Introduction

The Plains CO_2 Reduction (PCOR) Partnership, led by the Energy & Environmental Research Center (EERC), is one of seven regional partnerships in the United States funded by the U.S. Department of Energy's (DOE's) Regional Carbon Sequestration Partnership (RCSP) Program. As part of its ongoing regional characterization efforts, the PCOR Partnership has conducted a detailed examination of the potential CO_2 storage capacity of several stacked, brine-saturated formations in the vicinity of a cluster of six coal-fired power plants and one coal gasification plant in the North Dakota portion of the Williston Basin. The study area, referred to as the Washburn area, encompasses 15,900 km^2 and is home to six coal-fired power plants and one coal gasification plant which combine for annual emissions of over 32 million tonnes of CO_2.

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[1] Corresponding author. Tel.: +1-701-777-5393; fax: +1-701-777-5181.
E-mail address: yholubnyak@undeerc.org.

The Williston Basin is characterized by a thick sequence of sedimentary rock formations, in excess of 487 m at the basin center, which date from the Cambrian Period to the Holocene [1]. Deposition from the Cambrian Period through the lower Ordovician was predominantly siliciclastic (sandstone and shales). Carbonates (limestones and dolomites) and evaporites (anhydrites and salts) were the dominant lithologies from the middle Ordovician through most of the Mississippian. Siliciclastics again became the dominant lithology in the Pennsylvanian and remained so through the Holocene. The stratigraphy of the Williston Basin is illustrated in Fig. 1.

To evaluate potential chemical and physical reactions between pure CO_2 or a mixture of CO_2 and H_2S and selected Williston Basin rock units, samples representing five different formations were tested in bench-scale laboratory experiments. The comparison of the impact of the pure CO_2 versus acid gas (CO_2+H_2S) became a subtask for this project. Numerical modeling of geochemical reactions was performed and verified with laboratory results. The samples were chosen based on both core availability and on the likelihood of the formation being a target for future CO_2 storage.

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. A detailed description of each sample and its relevance as a potential carbon storage unit follows.

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 [2], five different formations were subjected to initial evaluation, and powdered rocks were used in order to obtain initial results. In this paper, authors present a further, more focused investigation of three different rock units: Madison Formation, Broom Creek Formation, and Tyler Formation (Fig. 2).

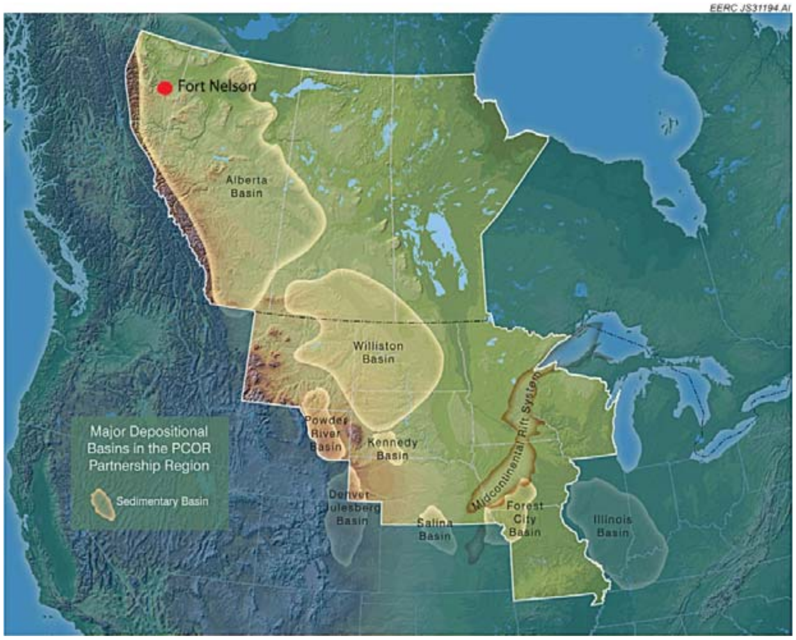

Figure 1 PCOR Partnership area and sedimentary basins.

The Madison Group is the primary oil-producing unit in the Williston Basin and provides significant opportunities for CO_2 sequestration through enhanced oil recovery [1]. The Madison is divided into three formations, which, in ascending order, are the Lodgepole, Mission Canyon, and Charles [3]. To evaluate potential interactions between CO_2 in the Mission Canyon Formation, a sample from a core was obtained. The combined mineralogical analysis suggests that major mineral phases in this sample are calcite (~60%), dolomite (~28%), anhydrite (~6%), quartz (less than 2%), illite (less than 2%), and pyrite (less than 1%). The minor mineralogical phases (less than 1%) were represented by chloride, fluorite, magnesite, and others.

Another representative of the Madison Group is the Mississippian–Ratcliffe Interval of the Charles Formation. This light gray limestone was recovered from the depth of 5895 ft (1797 m). This is almost uniformly light gray matrix (calcite), with minor inclusions of darker gray color. The sample is characterized by a smooth, nonporous texture. The combined mineralogical analysis suggests that the dominant phase is calcite (~75%), with dolomite (~11%), ankerite (~7%), quartz (less than 4%), and anhydrite (~1%).

The Pennsylvanian Tyler Formation is another oil-producing formation within the Williston Basin. The selected sample was recovered from a depth of 7968 ft (2429 m), and it is primarily clastic with a black, nonuniform structure with veins and spots of lighter and darker color. This sample

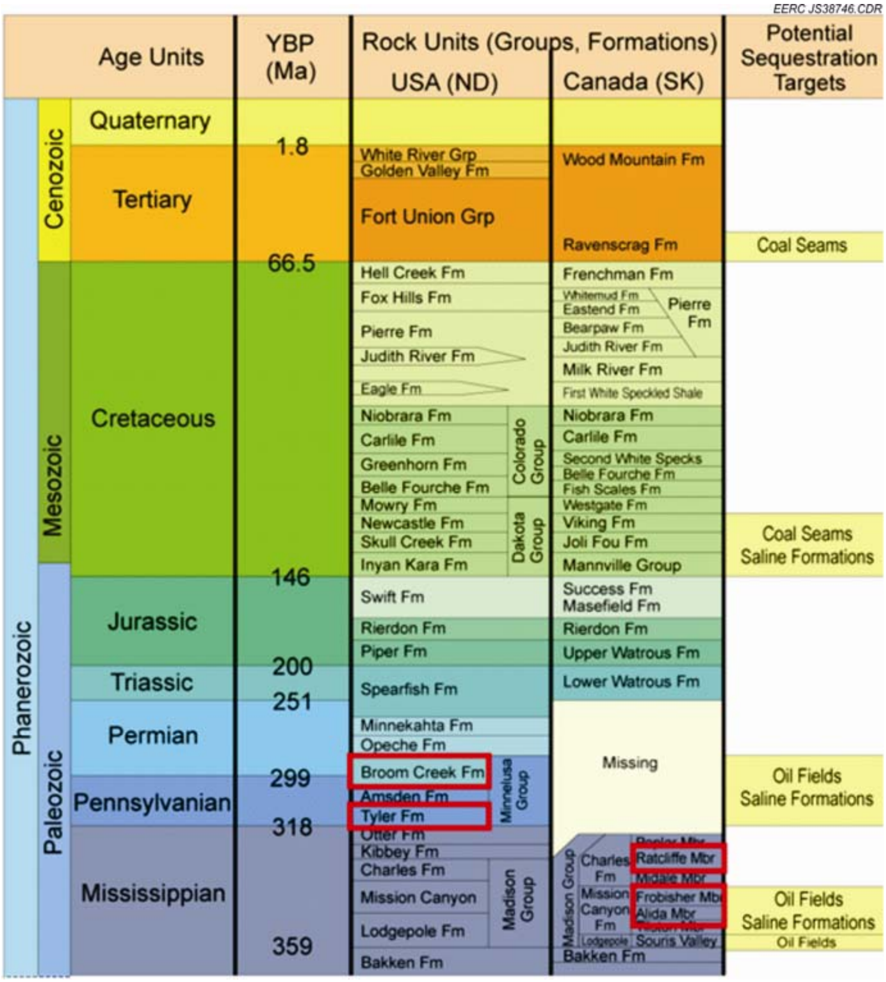

Figure 2 Stratigraphic column for the North Dakota portion of the Williston Basin with evaluated formations in red rectangles.

primarily consists of calcite (~50%) and quartz (~35%), with smaller amounts of many other minerals, such as muscovite, kaolinite, dolomite, anhydrite, albite, pyrite, and others. The mineralogical analysis of minor phases can be viewed as semiquantitative only, as the amounts of all minor phases were lower than 6%–7%.

The Broom Creek Formation is the thickest and most extensive brine-saturated sandstone in the Williston Basin, representing an excellent target for large-scale CO_2 storage. The Broom Creek Formation is the uppermost member of the three formations comprising the Minnelusa Group. The Broom Creek is characterized by porous and permeable fine- to medium-grained sands [4]. A sample of the Broom Creek Formation was obtained from a core that was extracted from a wellbore in Billings County at a depth of approximately 7800 feet. The sample appears as a white and red, subangular to rounded, fine-grained sandstone. The mineralogy analysis indicated quartz (~76%), illite (~13%), kaolinite (~6%), and pyrite (~2%) as primary mineral phases.

CO_2 Chamber Experiments

These experiments were designed to expose the selected rock/mineral samples to supercritical carbon dioxide under relatively high pressure and temperature, specifically 145.4 bar and 80°C, respectively (Table 1). The tests were conducted by placing a ½-in. core plug into a small scintillation vial and inserting the open vials into a reaction chamber, which could be regulated for temperature and pressurized with a CO_2 or combined CO_2 and H_2S atmosphere [5]. Each sample was simultaneously saturated with saline solution (sodium chloride – NaCl).

The samples were incubated in the testing chamber for a period of 4 weeks (28 days). The 4-week exposure time was conservatively selected after initial evaluation of the control sample (magnesium silicate) indicated that a complete reaction (carbonation reaction) was achieved after approximately 2 weeks [2].

Mineralogical Analysis

X-ray diffraction (XRD) analysis was performed on each sample after CO_2 exposure to determine the mineralogical components of the samples and to evaluate any physical or chemical changes. The XRD scans are utilized to identify mineralogical signatures and to qualitatively estimate major and minor sample constituents. In addition to analyzing the samples exposed to CO_2, a portion of the original sample was also analyzed to identify the original mineralogy.

Table 1 Experimental conditions

CO_2 and H_2S pressure:	145 bar
CO_2 partial pressure:	88 mol%
H_2S partial pressure:	12 mol%
Temperature:	80°C
Mass of sample	~7–15 g
Saturation conditions:	Synthetic brine: NaCl, 10% by weight
Time of exposure:	4 weeks

For the QEMSCAN analysis, samples of core plugs were prepared by placing a horizontal and a vertical section into a mold that was then filled with epoxy. After setting, the epoxy slug was cut to expose the sample and polished to an approximately 1-µm finish. Surficial reactions such as salt precipitation appear as a rind on the outside edges of a sample, whereas deeper reactions may be quantified by comparison to unreacted relative area percentages. Increases in phase definition to better examine trace concentrations of suggested reactive minerals within the matrix, specifically calcite/dolomite solutions, as well as added attention to rind composition should help to explain the reactions.

The integrative mineralogical analysis was performed utilizing linear program normative analysis (LpNORM). The computer code LPNORM implements the mathematical method of linear programming to calculate the mineralogical makeup of mineral mixtures, such as rock, sediment, or soil samples, from their bulk geochemical composition and from the mineralogical (or geochemical) composition of the contained minerals. This method simultaneously solves the set of linear equations governing the distribution of oxides into these minerals, subject to an objective function and a set of basic constraints [6].

Changes in brine composition as a result of mineral dissolution and precipitation were analyzed by inductively coupled plasma/mass spectrometry (ICP–MS).

Numerical Modeling

The numerical modeling was performed with PHREEQC [7] and Geochemist's Workbench (GWB) software packages. The kinetic rate parameters were selected from available literature sources [8] which describe pressure and temperature conditions in close proximity to the pressure and temperature conditions of the current experiment. Some of the listed kinetic rate parameters were not found in literature sources, so data that exist for similar minerals (e.g., minerals of the same group, similar crystal structure) were used instead. The sensitivity of the modeling because of this approximation is not known and requires further investigation. For improved modeling accuracy, the thermodynamic database for PHREEQC and GWB was recalculated and adjusted for the modeled set of pressure and temperature conditions with SUPRCRT92 code [9].

Results

After the 28 days of exposure to supercritical pure CO_2 or the CO_2+H_2S mixture, most samples were visibly altered. The changes apparent to the naked eye included obvious changes in porosity, coloration, crystal growth on the surface and fractures in fill, changes in water coloration, and water contamination by precipitated minerals (see Fig. 3). In some extreme cases, full or partial destruction of the sample was observed (e.g., Tyler Formation sample). There are several observations that are common for all investigated Williston Basin rocks: 1) relatively fast dissolution of carbonate minerals (calcite, dolomite, etc.); 2) mobilization of iron within carbonate, iron bearing and, possibly, clay minerals; 3) the reaction products are different for pure CO_2 and acid gas cases.

Carbonate Mineral Dissolution

For all investigated rocks from the Williston Basin, it was apparent that carbonate mineral dissolution has occurred. The dominant and fastest reaction was evidently the calcite dissolution. Different rocks from all four formations had different rates of carbonate dissolution; however, the

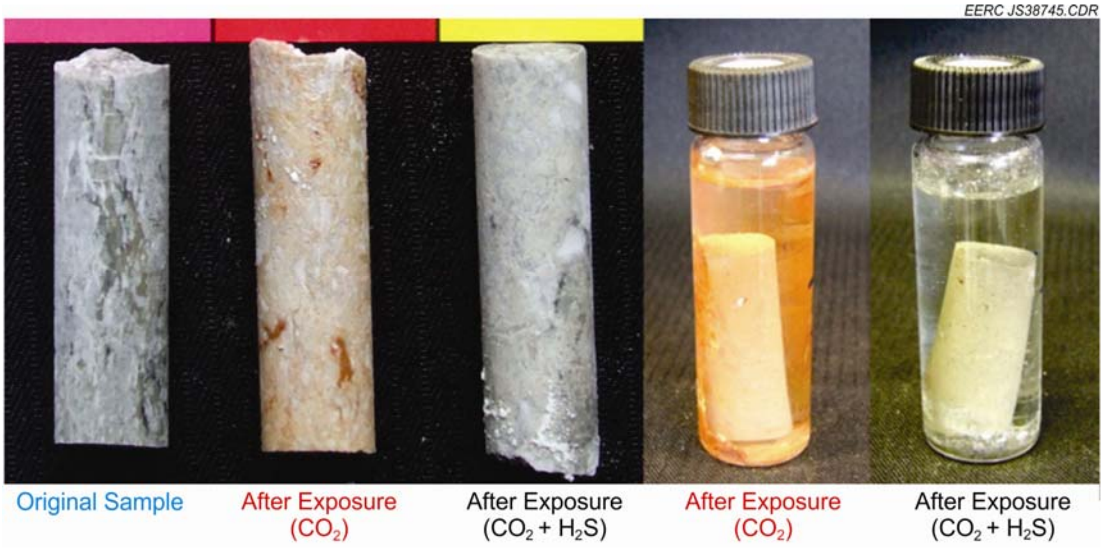

Figure 3 The Mississippian Mission Canyon sample collected from the depth of 2481 m was saturated with brine (NaCl, 10%) and exposed to pure supercritical CO_2 and a mixture of supercritical CO_2 (88 mole %) and H_2S (12 mole %) under pressure of 145.4 bar and temperature of 80°C. The left part of figure represents vacuum dried after exposure samples compared with the original specimen; and the right part illustrates samples saturated in fluid after the experiment completion.

difference in rates did not exceed 50%. For instance, after the 28 days of exposure to pure supercritical CO_2, the porous structure of the Frobisher–Alida rock became more prominent; the dark gray areas remained less porous and seem to have been affected less than the white and light gray areas. This observation correlates with the mineralogical analysis, which indicated that the dolomite dissolution was insignificant. In contrast, both QEMSCAN and XRD analysis shows the reduction in calcite content by more than 10%. In addition, the water analysis suggests that change in Ca content (1602 mg/L) must be attributed to calcite dissolution. The magnesium concentration (189 mg/L) in water was noticeably lower if compared to calcium and can be attributed to the Mg content naturally present in calcite minerals. These observations correlate with numerical modeling predictions very well (Fig. 4).

The visible increase in porosity and darker gray coloration are among changes in rock properties after exposure. The mineralogical analysis suggests the reduction in dolomite by more than 5%, which is supported by the water analysis where concentrations of Mg exceeded 350 mg/L for most samples (Fig. 4). Also, this observation was supported by the numerical modeling predictions, which correlate with laboratory measurements within a 10% error margin.

Summary and Suggestions for Future Developments

The analysis of obtained reaction products suggests that 1) there is no strong evidence for higher reactivity of samples exposed to the mixture of CO_2 and H_2S if compared to the pure CO_2 stream; however, 2) carbonate rocks seem to be more unstable when 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

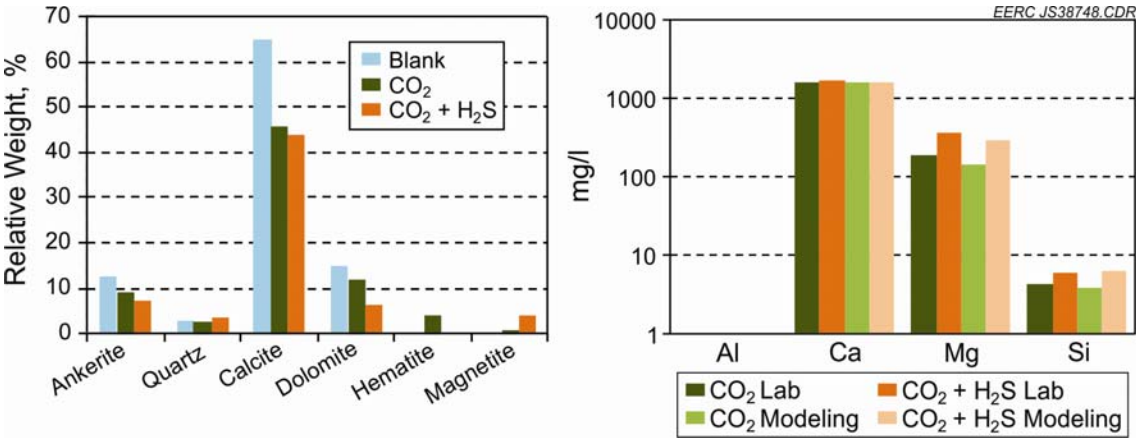

Figure 4 On the left: The combined mineralogical analysis of initial (unexposed) sample (blue color), sample exposed to CO_2 (dark green), and sample exposed to CO_2 and H_2S (orange). On the right: The exposed water composition analysis for metals compared to numerical modeling.

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

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