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## Investigation of Geochemical Interactions of Carbon Dioxide and Carbonate Formation in the Northwest McGregor Oil Field after Enhanced Oil Recovery and CO<sub>2</sub> Storage

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### Abstract

The Plains CO<sub>2</sub> Reduction Partnership, one of the seven U.S. Department of Energy National Energy Technology Laboratory Regional Carbon Sequestration Partnerships, is conducting a carbon dioxide (CO<sub>2</sub>) huff ‘n’ puff (HnP) project in the Northwest McGregor oil field in North Dakota to determine the effects CO<sub>2</sub> has on the productivity of the reservoir, wellbore integrity, and the carbonate formation into which the CO<sub>2</sub> was injected. This paper outlines the approach and current observations derived from numerical modeling and laboratory simulations of potential geochemical reactions to evaluate the short-term risks for operations (e.g., porosity and permeability decrease) and long-term implications for CO<sub>2</sub> storage via mineralization. The integration of data obtained during mineralogical analyses, fluid sampling, and laboratory experiments proved to be a key for the better understanding of the dynamic geochemical processes that happen in the reservoir after CO<sub>2</sub> injection and was necessary for successful completion of the numerical modeling. Results of the numerical modeling suggest that the already acidic and highly saline environment (pH <4.5 and total dissolved solids ~300,000 mg/kg) of the Northwest McGregor oil field should not experience any significant changes in mineralogy as a result of CO<sub>2</sub> injection, especially in the near term, which correlates with the postinjection field geochemical analyses.

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### Introduction

The Plains CO<sub>2</sub> Reduction (PCOR) Partnership regional characterization activities indicated that Williston Basin oil fields may have over 1.2 billion barrels of incremental oil that could be

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produced from CO<sub>2</sub> enhanced oil recovery (EOR) operations [1]. While the CO<sub>2</sub>-based EOR operations at the Weyburn and Midale Fields in Saskatchewan are good examples of economically and technically successful injection of CO<sub>2</sub> for simultaneous EOR and sequestration, the depths of injection and, therefore, reservoir conditions in those fields are relatively shallow (ca. 1400 m) and not necessarily representative of many large Williston Basin oil fields. One of the primary goals of the PCOR Partnership Phase II Williston Basin Field Validation Test was to evaluate the effectiveness of CO<sub>2</sub> for EOR and sequestration in carbonate oil fields at depths greater than 2400 m. To achieve that goal, a CO<sub>2</sub> HnP test was conducted in oil-producing well from an interval of the Mississippian age Madison Group at a depth of approximately 2450 m in the Northwest McGregor oil field in Williams County, North Dakota. The 440 tonnes of supercritical CO<sub>2</sub> was injected into a well over a 2-day period and allowed to “soak” for a 2-week period. The well was subsequently put back into production to recover incremental oil.

The main purpose of this study is to determine the effects CO<sub>2</sub> will have on the productivity of the reservoir and the carbonate formation into which CO<sub>2</sub> was injected. This paper outlines the approach for the numerical modeling and laboratory simulations of potential geochemical reactions and compares them with current field observations in order to evaluate the short-term risks for operations (e.g., porosity and permeability decrease) and long-term implications for CO<sub>2</sub> storage via mineralization.

### **Northwest McGregor Location and Geological Setting**

The Northwest McGregor oil field is located in Williams County in northwestern North Dakota, approximately 32 km north of the town of Tioga. The field covers an area of about 78 km<sup>2</sup> in an area of glaciated prairie uplands. Figure 1 shows the location of the Northwest McGregor oil field within the PCOR Partnership region and the relative locations of the E. Goetz No. 1 well, which served as the injection well, and the E.L. Gudvangen No. 1 well, which served as a deep observation well, within the Northwest McGregor oil field. Both oil wells are owned and operated by Eagle Operating Company, an independent oil company with headquarters in Kenmare, North Dakota.

The Northwest McGregor oil producing zone is in the Mississippian age Mission Canyon Formation (Figure 1), which represents deposition of predominantly carbonate sediments and evaporites in environments that ranged from open marine to coastal sabkha or salina [2, 3].

The E. Goetz No. 1 well was initially drilled in 1963, with production from the Mission Canyon beginning in 1964 and continuing through and beyond the time period of this project. Table 1 provides data on the initial reservoir conditions of the Northwest McGregor Mission Canyon Reservoir at the E. Goetz No. 1 location. It is important to note that the McGregor Mission Canyon Reservoir at the E. Goetz No. 1 location has very low matrix permeability and most of the fluid movement happens in fractures.

### **Reservoir Mineralogy**

Because the Mission Canyon Formation has been one of the most prolific producers of oil in the Nesson Anticline portion of the Williston Basin, it has been the subject of numerous technical papers and academic studies. With respect to the Northwest McGregor Field and its neighboring oil fields, there are bountiful data in well files that are publicly available through the North Dakota

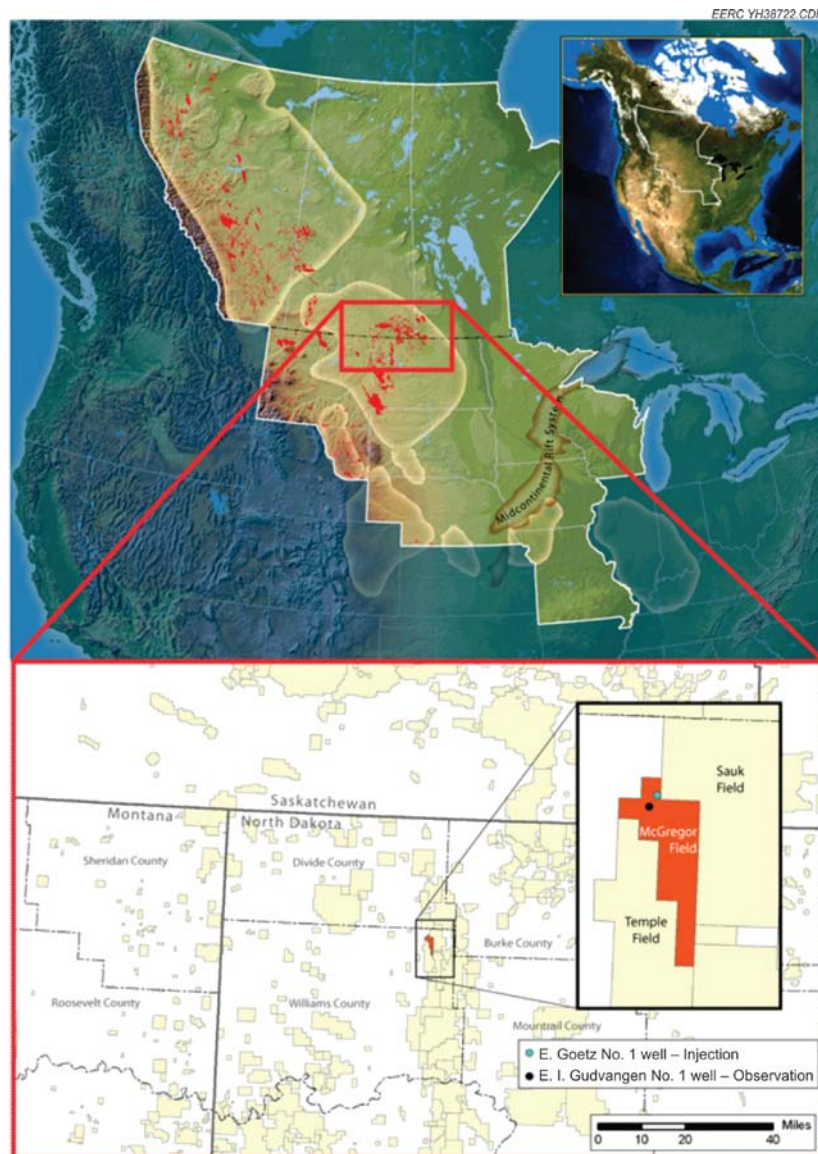


Figure 1 Location of Northwest McGregor site (red rectangle) within the PCOR Partnership region and the zoomed map view of the Northwest McGregor oil field with relative locations of the injection and observation wells.

Department of Mineral Resources. These papers, studies, and well files provide a tremendous amount of data regarding lithology, mineralogy, and formation fluid chemistry. However, in addition to well log analysis and in order to improve the accuracy of the geochemical modeling, available cuttings, core samples, and current reservoir fluid properties were analyzed.

The formation mineralogy, mineral composition, and the spatial variations at the Northwest McGregor site was determined using well logs, traditional core sample analysis with x-ray diffraction (XRD), x-ray fluorescence (XRF), and QEMSCAN<sup>TM</sup> techniques. All utilized techniques have certain advantages and disadvantages. For instance, XRD is usually considered to be a semiquantitative technique, and it is unable to identify phases below 1 to 5 wt%. If solid solutions are present or amorphous phases exist, it is very difficult to interpret the mineral assemblage. Therefore, the integrative mineralogical analysis was performed utilizing linear program normative

Table 1 Initial conditions of the Mission Canyon Reservoir of the Northwest McGregor oil field.

<b>Reservoir Characteristics</b>	
Producing Formation	Mission Canyon
Lithology	Limestone & Dolostone
Average Pay Thickness	4.27 m
Average Porosity	15%
Matrix Permeability	0.35 mD
Secondary Permeability	Fractures
Depth from Surface to Pay	2454 m
Average Temperature	102°C
Original Discovery Reservoir Pressure	21.6 MPa
Preinjection Reservoir Pressure	18.6 MPa
Oil Gravity (API)	41.7°
Cumulative Oil Production	2.2 million stock tank barrels

analysis (LpNORM) [4]. Using the results of these analyses, the mineral phases selected for model inputs were anhydrite, calcite, dolomite, illite, quartz, and traces of pyrite (Figure 2).

### Pre- and Postinjection Reservoir Fluid Analysis

The composition of the formation water is one of the critical inputs for geochemical modeling. However, the fluid analysis often becomes a very complicated matter because of the changing nature of gases and water at various pressures and temperature and the conditions of thermodynamic equilibrium in a changing environment.

Pre- and postinjection bottomhole samples were collected using Schlumberger's E-line tool and then transferred to Oilphase-DBR. The reservoir fluid and stock tank water (STW) properties for the before and after injection samples are presented in Figure 3. The gas from zero flash was subjected to ion chromatography, and its composition was determined for both samples (Figure 4). Other properties such as the physical properties of the STW were calculated and are listed in Table 2. The

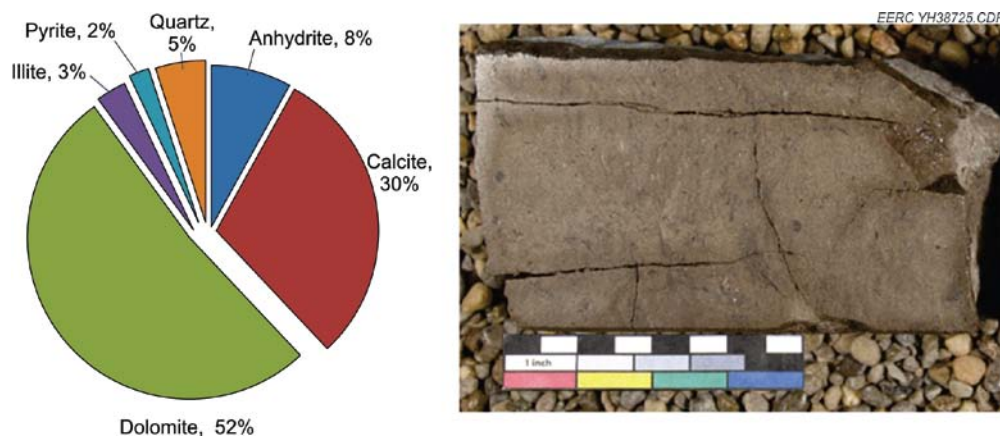


Figure 2 Mineralogical composition and an example of a core sample from the E. Goetz No. 1 well.

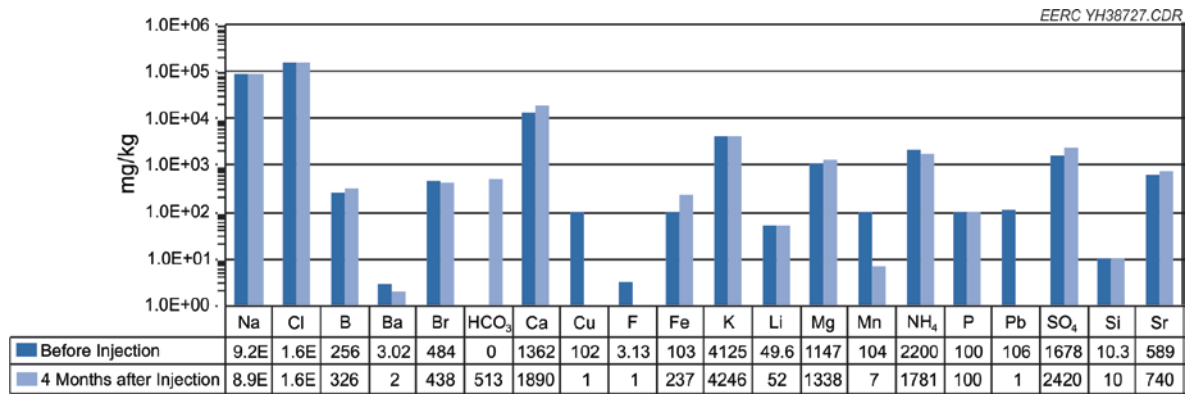


Figure 3 Extended comparison of pre- and postinjection reservoir fluid collected using Schlumberger's E-line from the depth of 2465 m at the E. Goetz No. 1 well, analyzed with Oilphase-DBR, and adjusted with the geochemical modeling software.

ion concentrations and other reservoir fluid properties (e.g., pH, ionic strength, etc.) were also modeled using PHREEQC and Geochemist's Workbench software packages and adjusted for correct reservoir pressure and temperature.

The Oilphase-DBR live pH measurement technique uses pH-sensitive dyes that change color according to the pH of the formation water. The live water pH technique was applied for the preinjection sample analysis only. Upon injection of dye into the sample at reservoir pressure and temperature, it was determined that the pH value of the sample is expected to be <4.5 units at 17.9 MPa and 107°C.

### Major Observations and Comparison of the Reservoir Fluid Sampling

The key observations from the field-based data are 1) the displacement of the H<sub>2</sub>S gas by CO<sub>2</sub> around the wellbore; 2) an increase in TDS as a result of some mineral dissolution, in particular the Ca and Sr concentration increase, which can be explained by the limestone dissolution; and 3) a further pH decrease due to CO<sub>2</sub> dissolution.

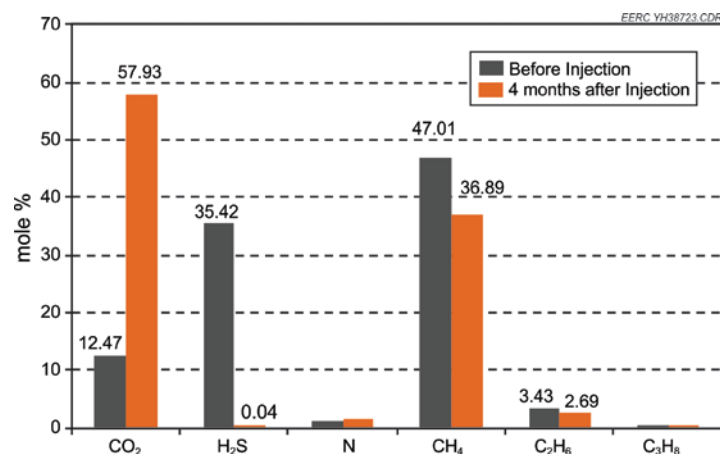


Figure 4 Comparison of pre- and postinjection reservoir gas compositions from zero flash and subjected to chromatography from the depth of 2465 m. at the E. Goetz No. 1 well.



Table 2 Comparison of pre- and postinjection reservoir fluid collected using Schlumberger's E-line from the depth of 2465 m from the E. Goetz No. 1 well and analyzed with Oilphase-DBR.

	pH	Density, g/cm <sup>3</sup>	Resistivity at 25°C, Ω	Salinity, mg/kg	TDS, <sup>a</sup> mg/kg
Before Injection	5.55 (at 41°C) 4.50 (at 102°C – live pH) 4.23 (modeled)	1200	4.02	283855	273353
After Injection	5.4 (at 41°C) 3.1 (modeled)	1208	4.17	282925	276477

<sup>a</sup> Total dissolved solids.

## Laboratory Experimentations

The series of laboratory experiments and numerical modeling of geochemical reactions were conducted. Core samples collected from Mississippian Mission Canyon Formation of the Williston Basin were exposed for a period of 4 weeks to pure supercritical carbon dioxide at 15.5 MPa and 70°C in 10 wt% NaCl synthetic brine conditions. Prior to exposure, XRD and XRF mineralogical analysis demonstrated the presence of ankerite, anhydrite, calcite, dolomite, halite, illite, pyrite, and quartz. After exposure, mineralogical (XRD and QEMSCAN) and water analysis (inductively coupled plasma–mass spectroscopy) were also performed. The laboratory observations were later correlated with the field data and numerical modeling (Figure 5).

Observations made during the laboratory experiments were in good correlation with field observations and illustrated the dissolution of the carbonate rocks. In addition, insignificant amounts of hematite precipitation due to iron mobilization was observed (Figure 5).

## 2-D Reservoir Geochemical Modeling with GEM

The reservoir simulation model was created according to generalized uniform reservoir parameters: pressure of 20.7 MPa; in situ gas composition of CO<sub>2</sub> at 12.5%, CH<sub>4</sub> at 47%, H<sub>2</sub>S at 35.5%, porosity

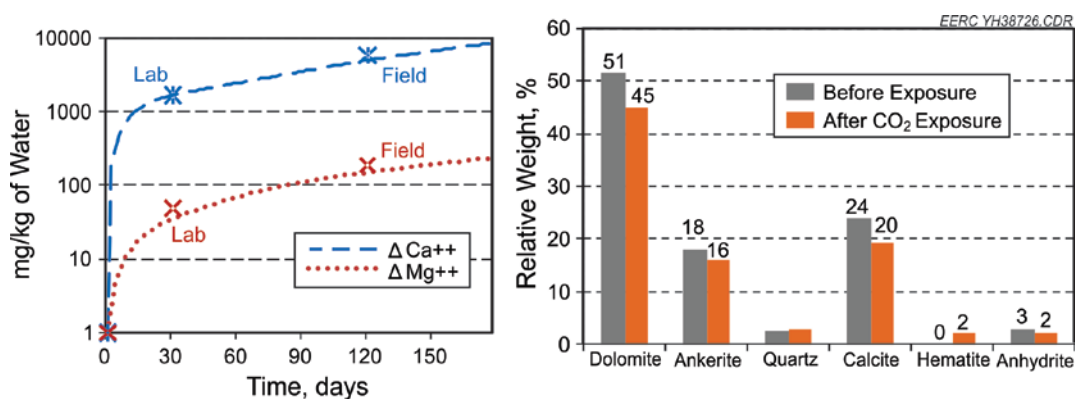


Figure 5 The Mississippian Mission Canyon sample was saturated with synthetic NaCl brine and exposed to supercritical CO<sub>2</sub> at the reservoir conditions. Changes in concentration of Ca and Mg are modeled and correlated with field and laboratory observations (left) and mineralogical changes (right).

of 15%, permeability of 35 mD, and water saturation of near 1. The permeability of 35 mD was picked to compensate the movement in fractures, which was not implemented in this exercise for time-saving purposes, and is planned to be implemented in the next set of calculations. The reservoir thickness was assumed to be 9.1 m. The carbon dioxide was injected into a grid block, which offset the boundary layer by 0.9 m. The simulation run included calcium and dolomite minerals and did not account for hematite precipitation. The time line for the modeling exercise was chosen as 10 years based on the preliminary kinetic numerical modeling with PHREEQC and Geochemist's Workbench. The dissolution of carbonate minerals was illustrated and, as a result of dissolution, the increase in porosity was modeled (Figure 6).

## Summary and Conclusions

The integrated investigation of field and laboratory data and numerical modeling exercises revealed that no significant changes in reservoir geochemistry have accrued. The small porosity increase might have contributed to the improved oil production from the E. Goetz No. 1 well. Laboratory studies and numerical modeling suggests that CO<sub>2</sub> trapping by mineralogical processes is minimal for the Northwest McGregor oil field EOR case. The high concentration of salts in the formation fluid and the already very acidic environment of the Mission Canyon Reservoir are likely the primary factors contributing to the minimal geochemical response of the Northwest McGregor Reservoir to the injected CO<sub>2</sub>.

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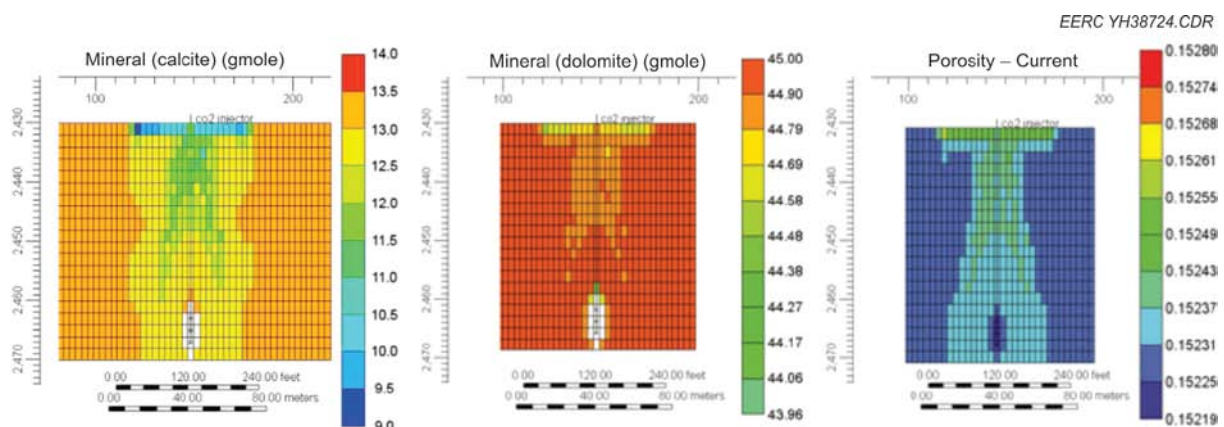


Figure 6 Spatial 2-D distribution of the calcite and dolomite dissolution and insignificant porosity increase modeled 10 years after the injection.

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