### PS Geochemical Modeling of Carbon Dioxide Injection into Carbonate Formation in the Northwest McGregor Oil Field for CO<sub>2</sub> Storage and Enhanced Oil Recovery (EOR)\*

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### **Abstract**

Injection of carbon dioxide (CO<sub>2</sub>) for the purpose of enhanced oil recovery (EOR) is widely regarded as one of the key commercial applications of geological storage that will provide valuable insight into large-scale projects aimed at reducing CO<sub>2</sub> emissions to the atmosphere. The Plains CO<sub>2</sub> Reduction Partnership, one of the seven U.S. Department of Energy National Energy Technology Laboratory Regional Partnerships, is conducting a project in the Northwest McGregor oil field in North Dakota to determine the effects CO<sub>2</sub> will have on the productivity of the reservoir, wellbore integrity, and the carbonate formation into which CO<sub>2</sub> was injected. The method used in this project is "huff 'n' puff" whereby 400 tons 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. Then the well was subsequently put back into production to recover incremental oil.

The purpose of this paper is to outline the approach and current observations for the numerical modeling of potential geochemical reactions 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. Mineralogy of the reservoir was determined using well logs, traditional core sample analysis, x-ray diffraction, and QEMSCAN techniques. Using the results of these analyses, the mineral phases selected for model inputs were anhydrite, calcite, dolomite, illite, K-feldspar, and traces of pyrite. A pressurized bottom-hole fluid sample was also collected, and its composition was determined. The results of this fluid sample were also used as input parameters for the model.

Modeling was performed using PHREEQC and Geochemist Workbench software in order to determine the most favorable geochemical interactions, evaluate in situ fluid properties, etc. The Computer Modeling Group Ltd. GEM simulator was utilized for

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the creation of a 2-D cross-section model for reactive transport evaluation. It was determined that the already reducing environment of the Northwest McGregor oil field should not experience any significant changes in mineralogy, especially in the near term. However, the possibility of minor reprecipitation of pyrite and precipitation of siderite exists. Also, the long-term (over 10,000 years) dissolution of calcite with a following precipitation of gypsum and dolomite may occur.



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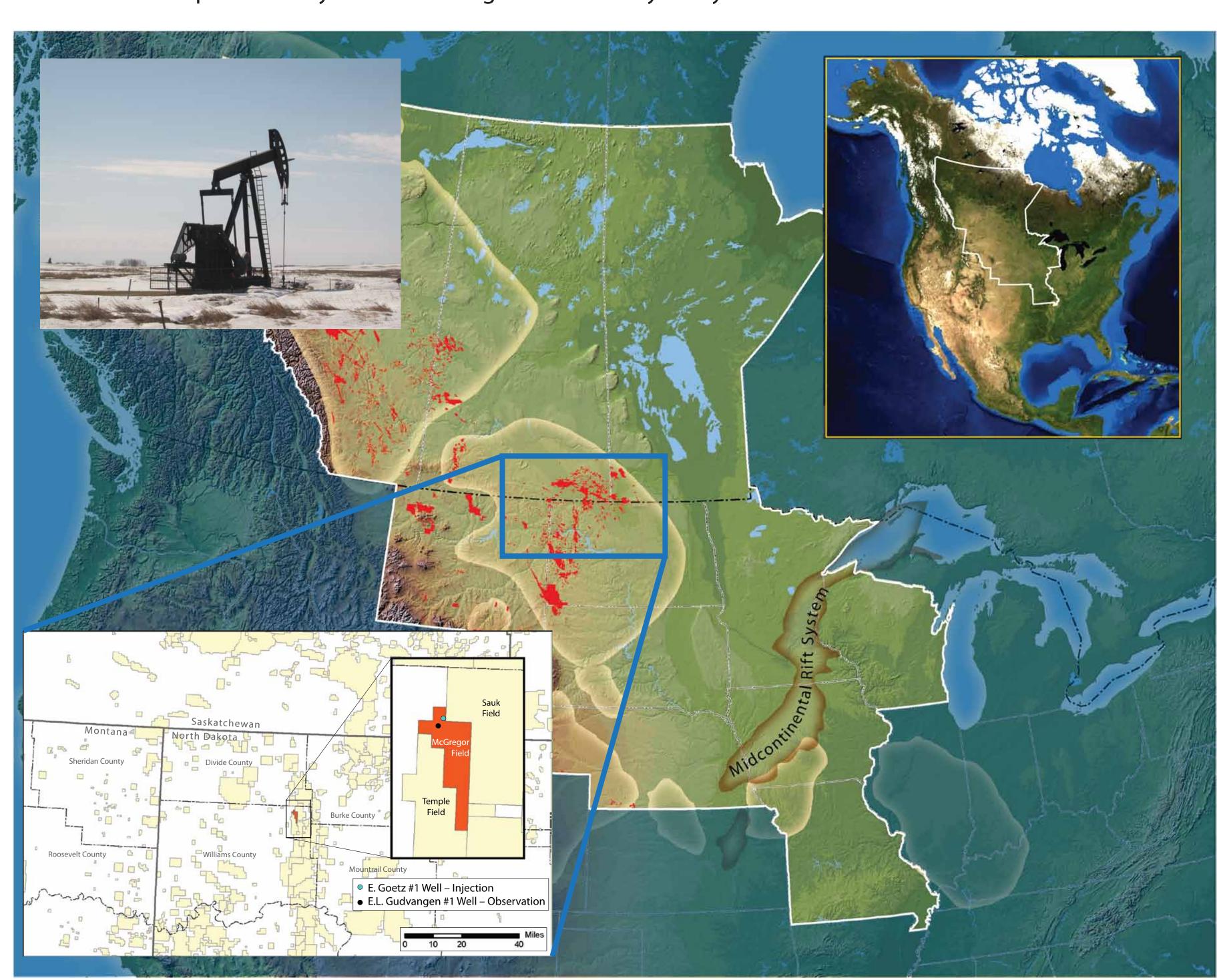
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# ABSTRACT

Injection of carbon dioxide (CO<sub>2</sub>) for the purpose of enhanced oil recovery (EOR) is widely regarded as one of the key commercial applications of geological storage that will provide valuable insight into large-scale projects aimed at reducing CO<sub>2</sub> emissions to the atmosphere. 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 project in the Northwest McGregor oil field in North Dakota to determine the effects CO<sub>2</sub> will have on the productivity of the reservoir, wellbore integrity, and the carbonate formation into which CO<sub>2</sub> was injected. The method used in this project is huff 'n' puff whereby 400 tons 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. Then the well was subsequently put back into production to recover incremental oil.

The purpose of this paper is to outline the approach and current observations for the numerical modeling of potential geochemical reactions 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. Mineralogy of the reservoir was determined using well logs, traditional core sample analysis, x-ray diffraction, and QEMSCAN techniques. Using the results of these analyses, the mineral phases selected for model inputs were anhydrite, calcite, dolomite, illite, K-feldspar, and traces of pyrite. A pressurized bottom-hole fluid sample was also collected, and its composition was determined. The results of this fluid sample were also used as input parameters for the model.

Modeling was performed using PHREEQC and Geochemist Workbench software in order to determine the most favorable geochemical interactions, evaluate in situ fluid properties, etc. The Computer Modelling Group Ltd. GEM simulator was utilized for the creation of a 2-D cross-section model for reactive transport evaluation. It was determined that the already-reducing environment of the Northwest McGregor oil field should not experience any significant changes in mineralogy, especially in the near term. This conclusion is also supported by a laboratory study, which is presented in this poster. Minor calcite and dolomite dissolution is predicted by both modeling and laboratory study.



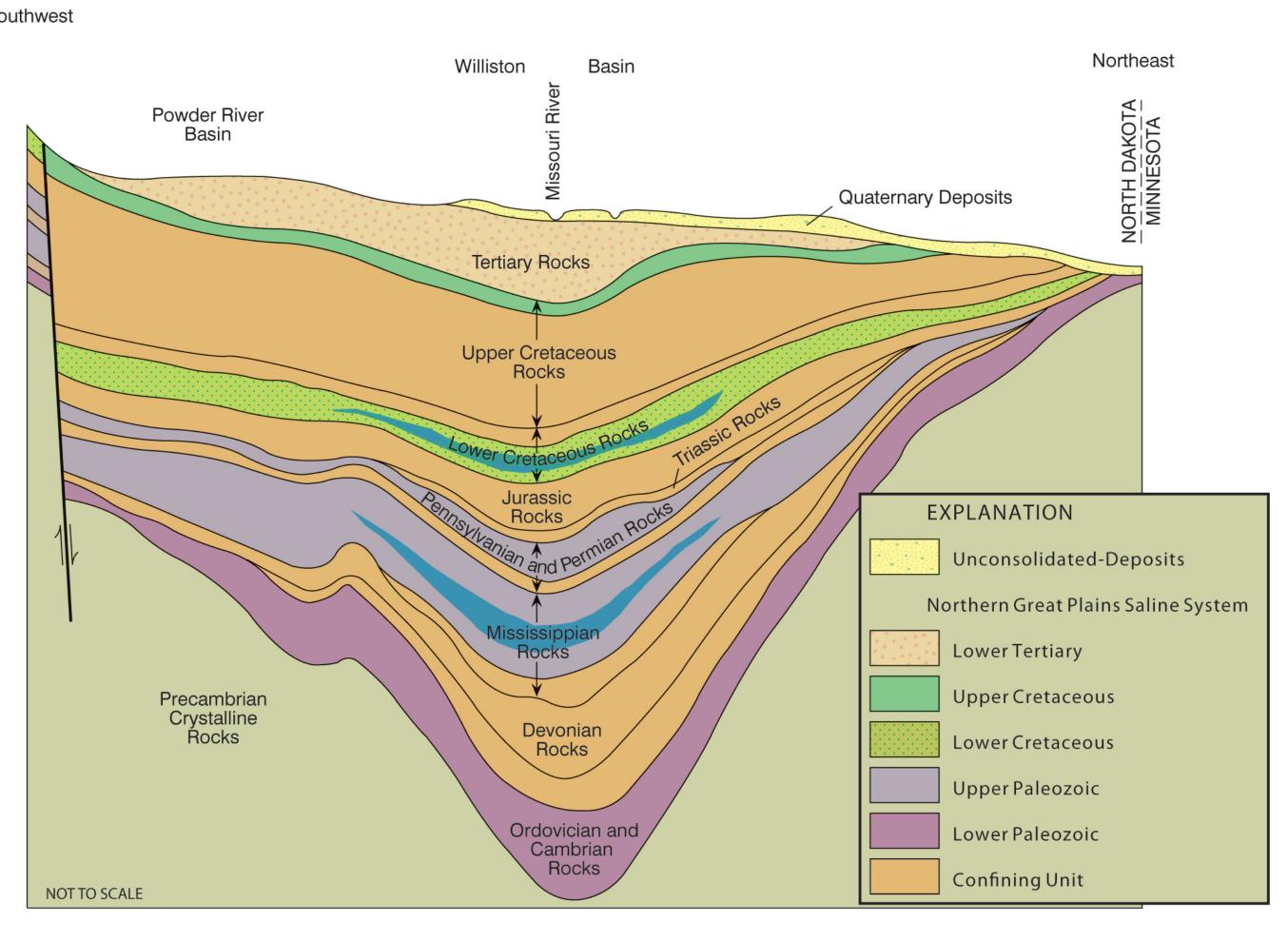




# RESERVOIR CHARACTERISTICS

| Producing Formation                   | Mission Canyon      |  |  |
|---------------------------------------|---------------------|--|--|
| Lithology                             | Primarily Limestone |  |  |
| Average Porosity                      | 15%                 |  |  |
| Matrix Permeability                   | 0.35 mD             |  |  |
| Secondary Permeability                | Fractures           |  |  |
| Depth from Surface to Pay             | 8050 ft/2434 m      |  |  |
| Average Temperature                   | 216°F/102°C         |  |  |
| Original Discovery Reservoir Pressure | 3127 psig/216 bar   |  |  |
| Preinjection Reservoir Pressure       | 2700 psig/186 bar   |  |  |
| Oil Gravity (API)                     | 41.7°               |  |  |
| Cumulative Oil Production             | 2.2 million STB     |  |  |
|                                       | -                   |  |  |

## RESERVOIR LOCATION



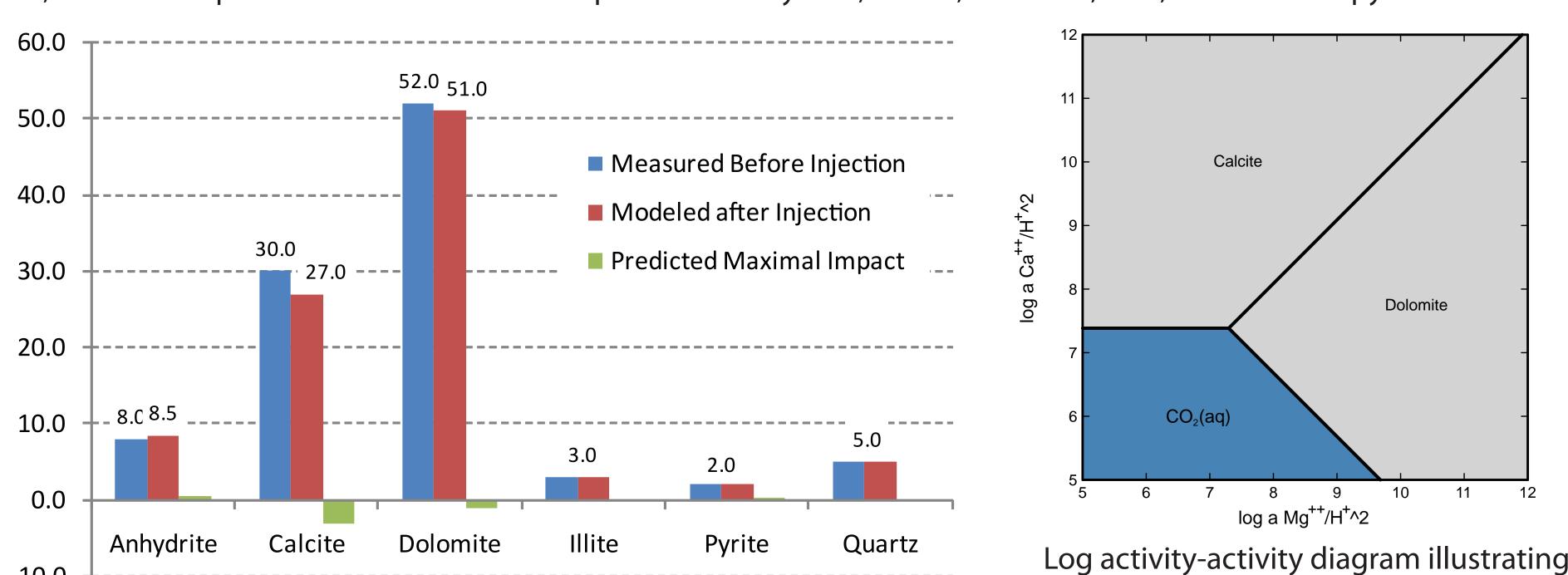
| Age Units   |           | Ane Units     | (Ma)       | Rock Units (Groups, Formations)  |  | Hydrogeologic<br>Systems <sup>3</sup>  |  | Sequences <sup>4</sup>                 | Potential Sequestration |  |
|-------------|-----------|---------------|------------|--|--|--|--|--|-------------------------|--|
|             |           | 7 tgc 0111t3  | (Ma)       | USA <sup>1</sup> (ND   | ))   | Canada <sup>2</sup> (SK)   | USA  | Canada                                 | Dequences               | Targets                                      |
|             |           | Pennsylvanian |            | Broom Creek Fm  Amsden Fm  Tyler Fm  | Minnelusa<br>Group   | Missing  | AQ3<br>Aquifer   | Mississippian-<br>Jurassic<br>Aquitard | Absaroka                | Oil Fields<br>Saline Formations              |
| Phanerozoic | Paleozoic | Mississippian | 318        | Otter Fm<br>Kibbey Fm<br>Charles Fm  | on<br>d  | Charles Ratcliffe Mbr Fm Midale Mbr  | TK2<br>Aquitard  | System                                 |                         |  |
|             |           |               |            | Mission Canyon  Lodgepole Fm   | Madison<br>Group   | Mission Frobisher Mb Canyon Alida Mbr Fm Tilston Mbr Lodgepole Souris Valley | AQ2 or<br>Madison<br>Aquifer   | Mississippian<br>Aquifer<br>System     | Kaskaskia               | Oil Fields<br>Saline Formation<br>Oil Fields |
|             |           | Devonian      | 359<br>416 | Bakken Fm Three Forks Birdbear Duperow Souris River Dawson Bay Prairie Winnipegosis Ashern | Bakken Fm Big Valley Fm Three Forks Birdbear Duperow Souris River Dawson Bay Prairie Winnipegosis Ashern | TK1<br>Aquitard  | Bakken Aquitard Devonian Aquifer System Prairie Aquiclude Winnipegosis Aquifer |  | Oil Fields              |  |
|             |           |               | 410        |  |  |  |  |  |                         |  |

# OPERATIONAL PARAMETERS

| OPERATIONAL PARAIVIETERS |   |                   |  |  |  |
|--------------------------|---|-------------------|--|--|--|
|                          | Total Mass of CO <sub>2</sub> Injected                          | 440 tons          |  |  |  |
|                          | Maximum Allowable Injection Pressure Based on Fracture Gradient | 5100 psig/352 bar |  |  |  |
|                          | Average Injection Rate  | 12.2 tons/hour    |  |  |  |
|                          | Average Injection Pressure (surface)                            | 2900 psig/200 bar |  |  |  |
|                          | Average Injection Pressure (bottomhole)                         | 5000 psig/345 bar |  |  |  |
|                          | Average Injection Temperature (bottomhole)                      | 190°F/88°C        |  |  |  |
|                          | Wellhead Pressure at End of Injection                           | 3500 psig/341 bar |  |  |  |
|                          | Length of Injection Period                                      | 36 hours          |  |  |  |

# MINERALOGY ANALYSIS

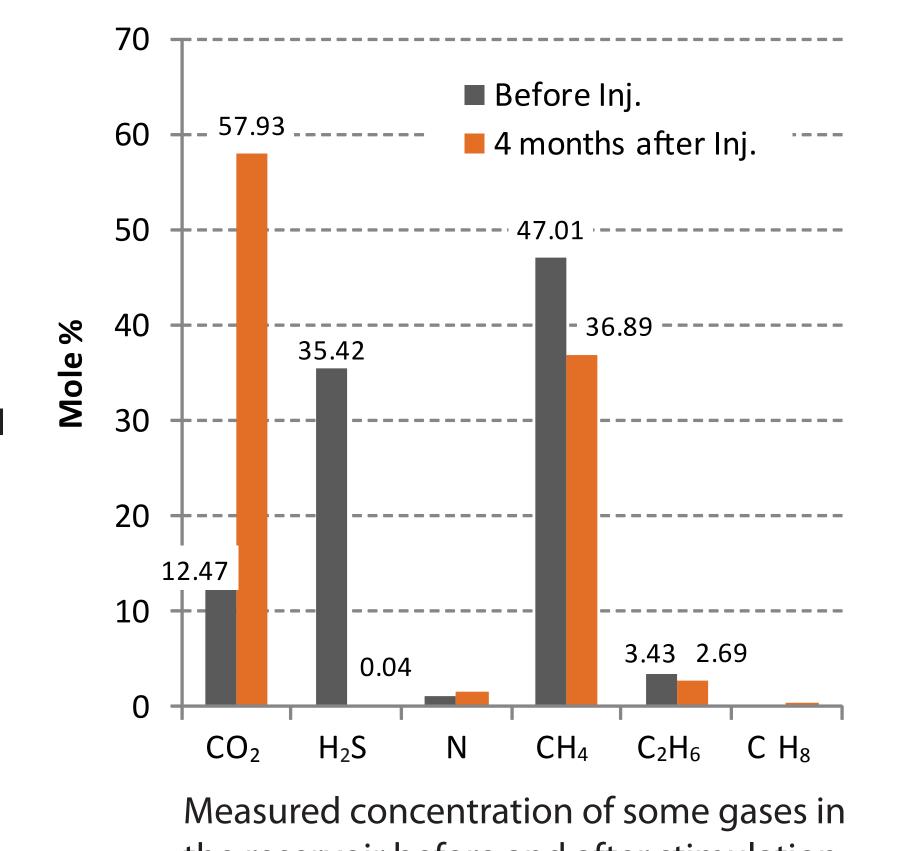
The formation mineralogy, mineral composition, and the spatial variations at the Norwest McGregor site were determined using well logs, traditional core sample analysis with XRD, XRF, and QEMSCAN techniques. All utilized techniques have certain advantages and disadvantages. For instance, XRD diffraction is usually considered to be a semiquantitative technique, and it is unable to identify phases below 1 to 5 weight percent, and 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 analysis (LpNORM). Using the results of these analyses, the mineral phases selected for model inputs were anhydrite, calcite, dolomite, illite, and traces of pyrite.



# FLUID SAMPLE ANALYSIS

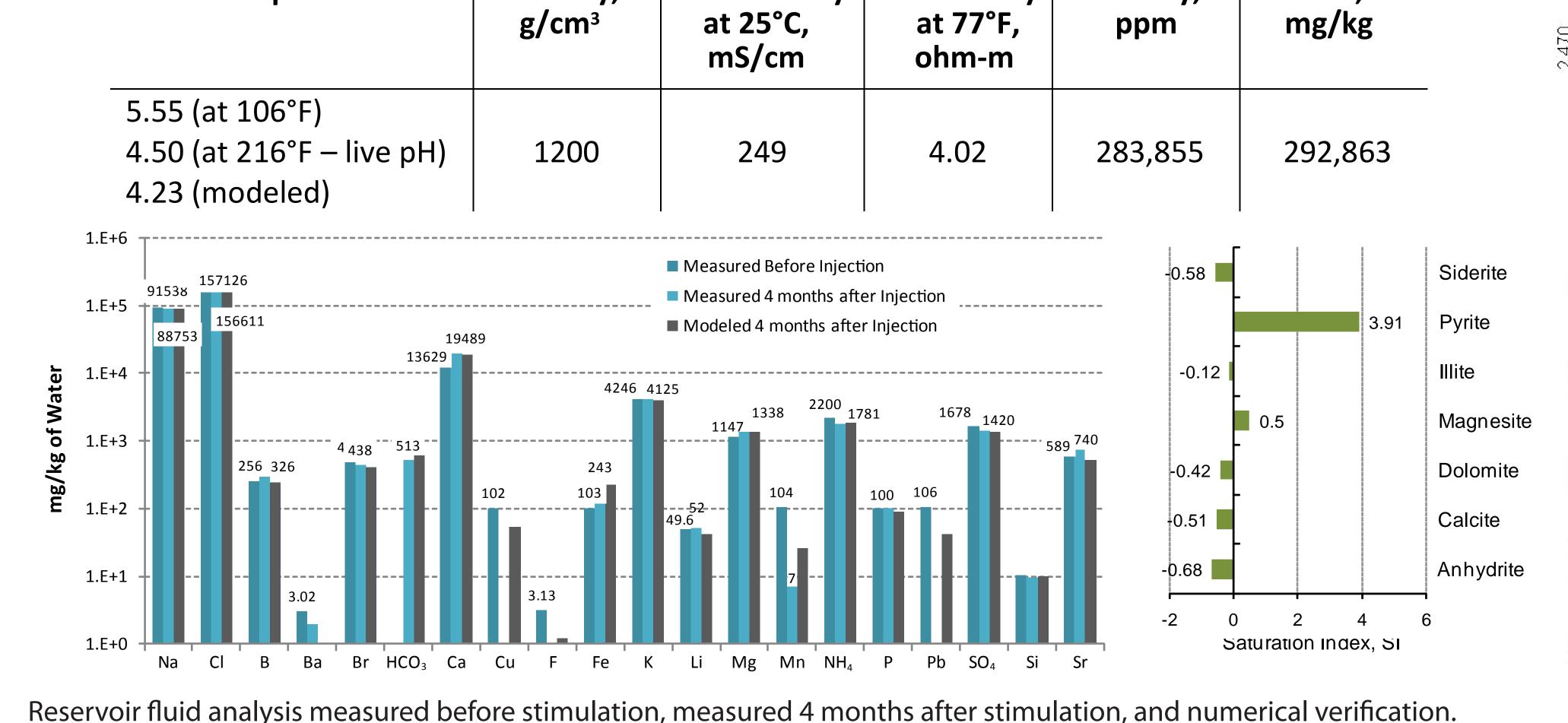
A single bottomhole sample collected using Schlumberger's E-line was transferred to Oilphase-DBR. The gas from zero flash was subjected to chromatography, and its composition was

The live water pH measurement service offered by Oilphase DBR is an extension of the already-commercial downhole pH measurement service. Both the techniques overcome the limitations of the traditional practice of flashing high-temperature, high-pressure water (HTHP) to room temperature and conventional  $\geq$  30 +-analysis of flashed gas and water at ambient conditions. These traditional analyses of flashed gas and water are used as inputs to calculate HTHP pH by chemical equilibrium modeling. This technique introduces errors in pH because of sample handling, precipitation of ionic solids from flashed water samples, and the modeling uncertainties of complex ionic equilibrium. By taking the measurements at the HTHP state, these errors are eliminated On 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 2600 psia and 225°F.

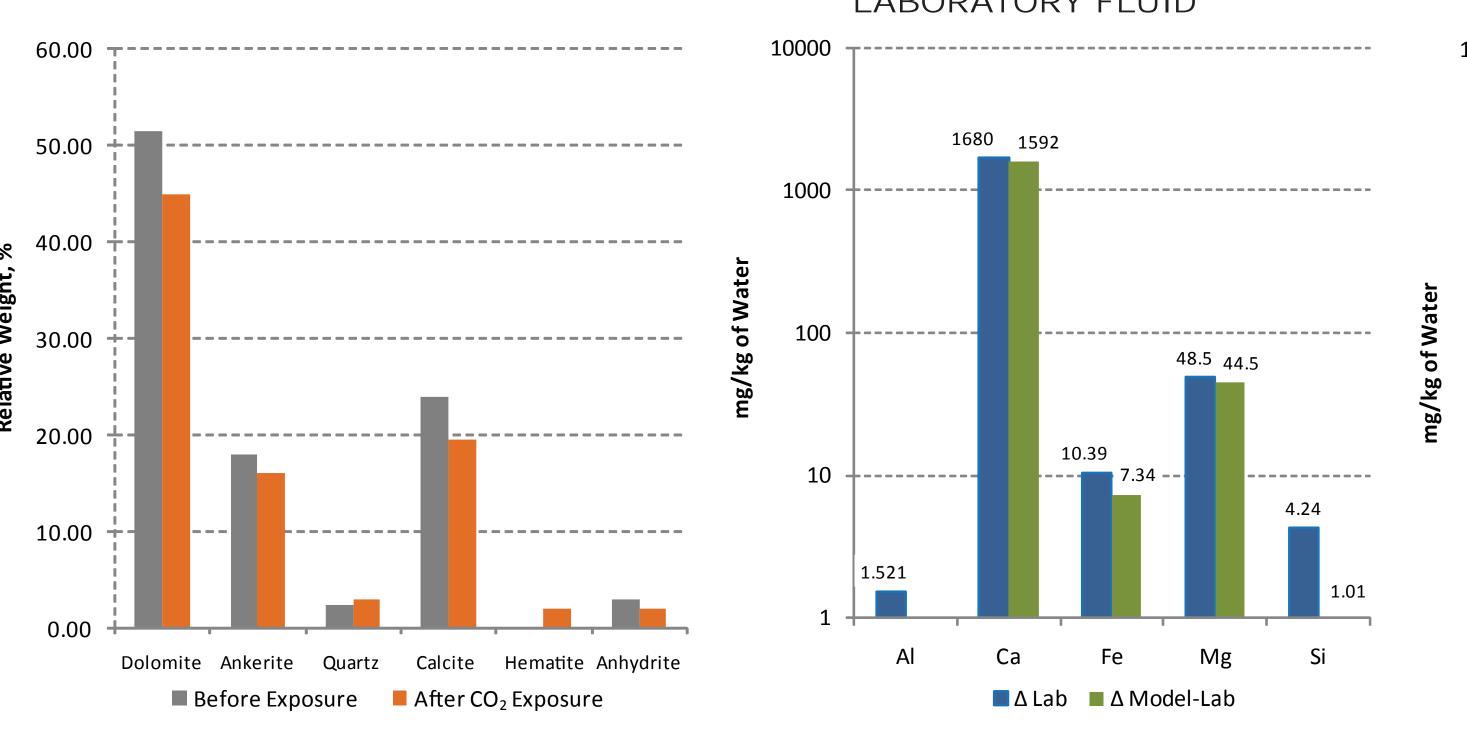


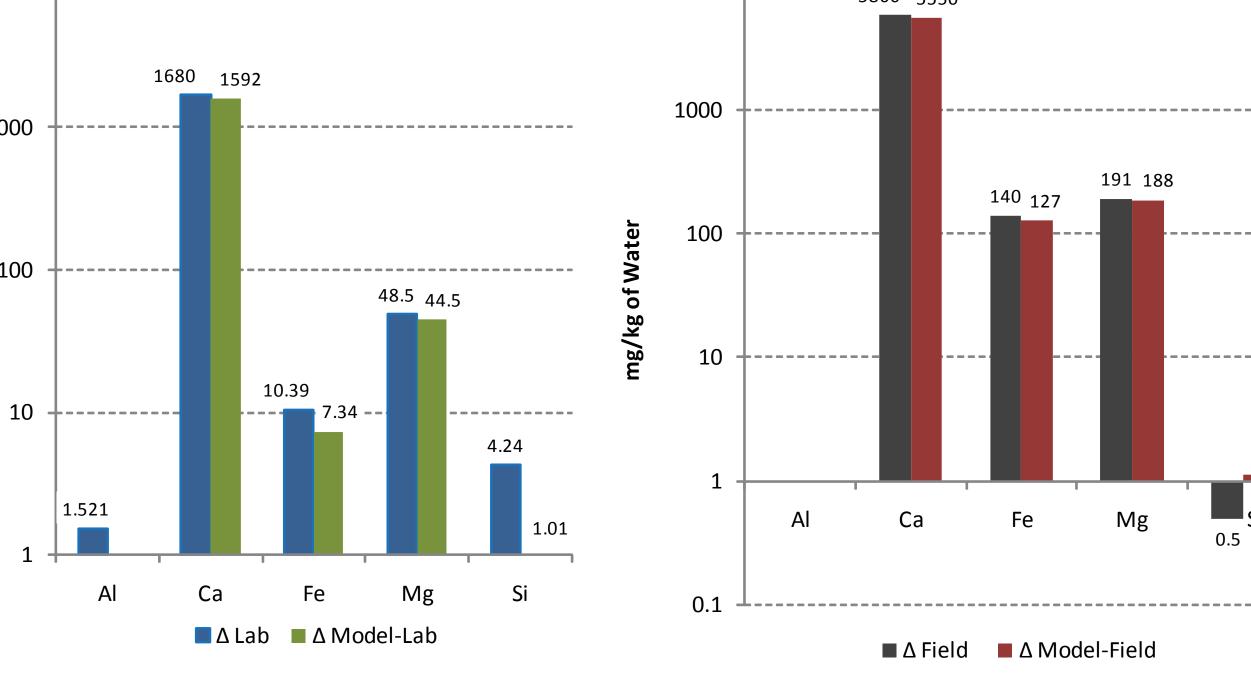
the stability of calcite and dolomite.

the reservoir before and after stimulation





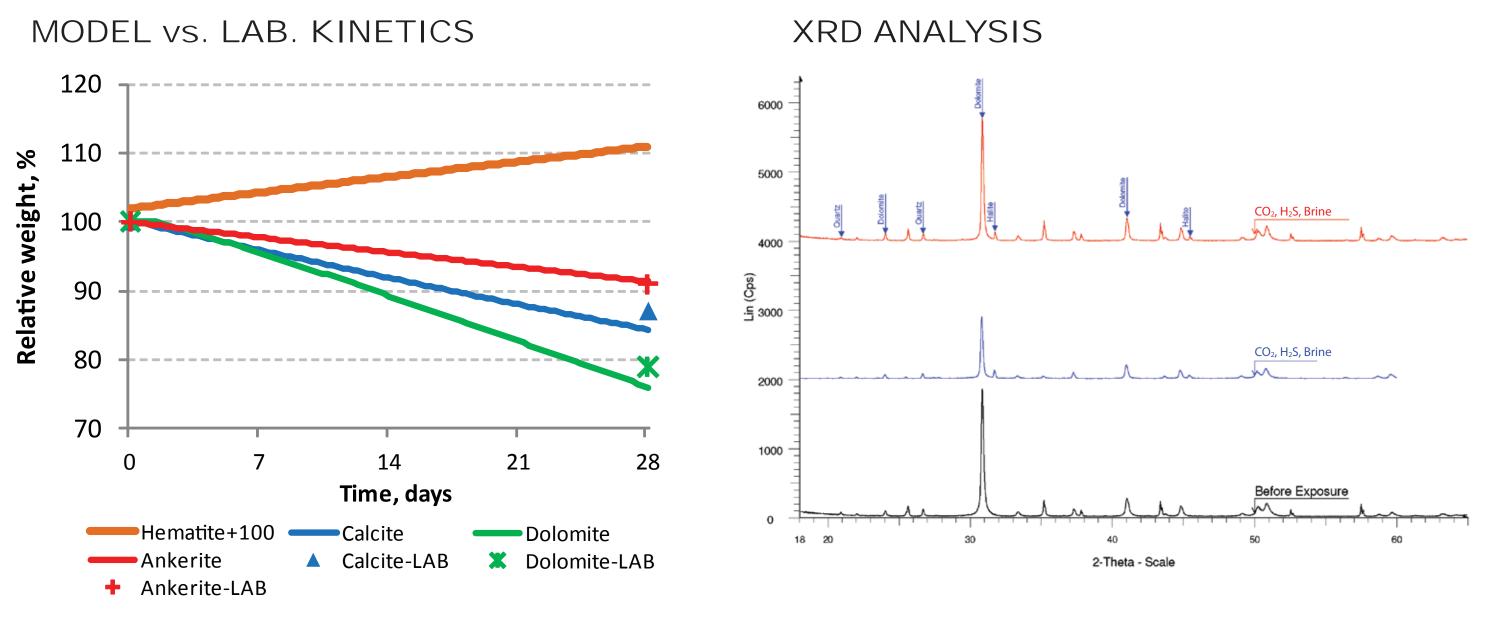




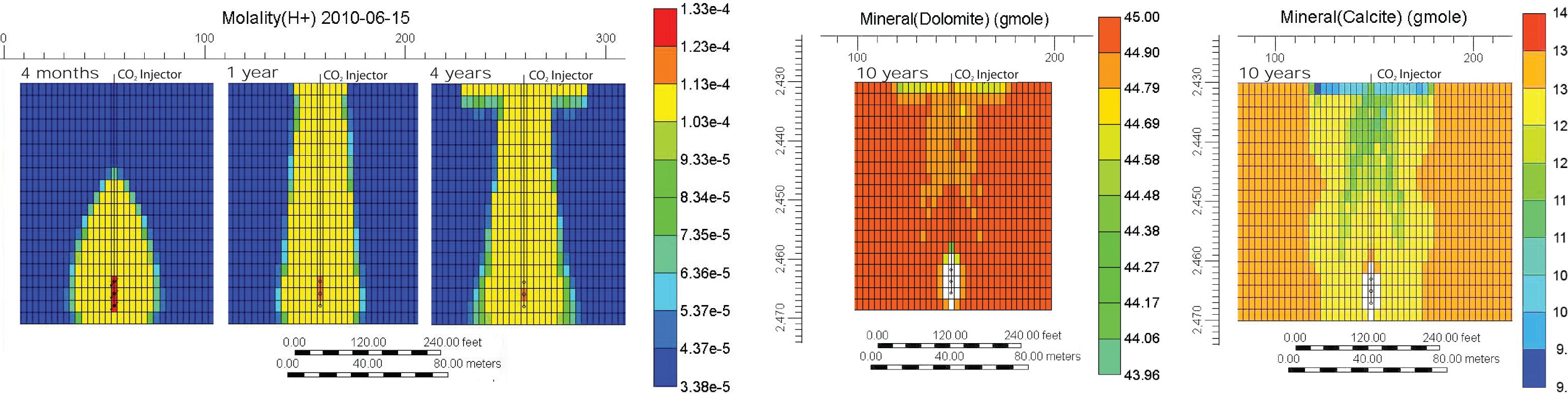
Comparison of changes in fluid compositions before and after stimulation. Normilized mineralogical analysis.

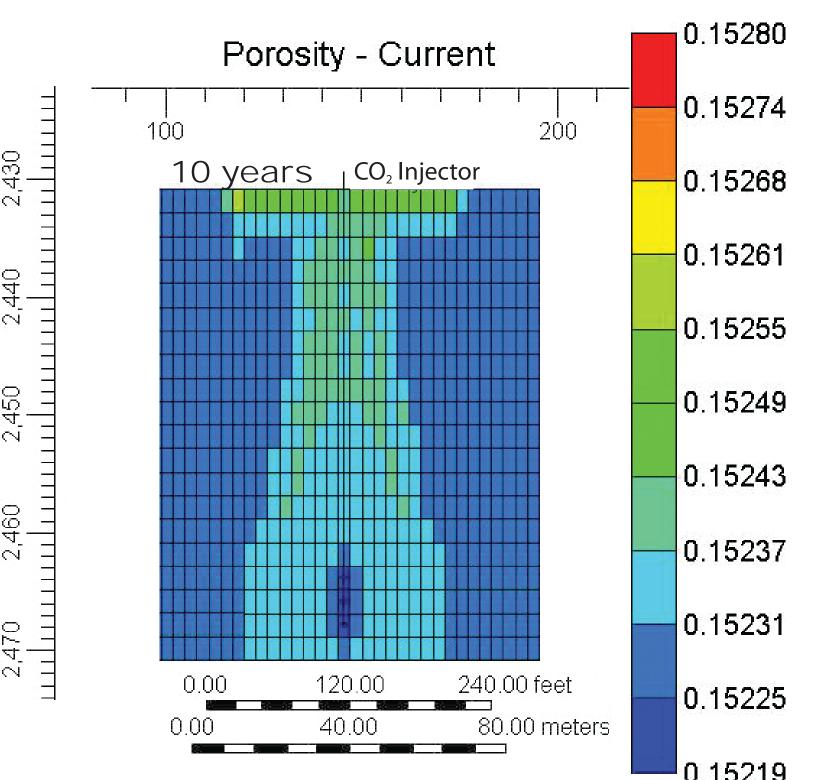
The experiments were designed to expose the selected rock/mineral samples to CO<sub>2</sub> under relatively high pressure and temperature, specifically 2100 psi or 145.4 bar and 176°F or 80°C, respectively. The tests were conducted by placing core plug into a small (15-mL) scintillation vial and inserting the  $\frac{3}{4}$ open vials into a chamber, which could be regulated for temperature and pressurized with CO<sub>2</sub>. 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. Comparative methodology using the XRD, XRF, and QEMSCAN techniques was utilized.



# 2-D RESERVOIR MODEL





- The fluid samples recovered before and after CO<sub>2</sub> injection with the Schlumberger's E-line technique and analyzed by Oilphase-DBR and various geochemical modeling techniques illustrated:
- Unusually low (< 4.5) pH readings
- Very consistent dataset which proved to be viable and applicable for further modeling assemblage
- Very high concentration of dissolved solids (around 300,000 mg/kg of water)
- Results of the equilibrium modeling further indicated that the analyzed water is in equilibrium or near-equilibrium state with the Mississip pian formation minerals: anhydrite, calcite, dolomites, pyrite, and illite.
- 3. Modeling suggests low reactivity of the reservoir rocks with the injected CO₂ and in situ brine. However, minor mineralogical changes are predicted to occur: the dissolution of calcite and dolomite minerals. The kinetic and mass transfer modeling illustrated the dynamics of the possible mineralogical changes. It was observed that the next thermodynamically stable point can be reached almost 7 years after CO<sub>2</sub> injection.
- The numerical modeling results are in agreement with laboratory studies. In addition, low precipitation of hematite was observed in laboratory conditions, as a result of minor ankerite dissolution.