PS Investigation of Potential Geochemical Reactions in Large-Scale Carbon Dioxide-Enhanced Oil Recovery (CO_2-EOR) Carbonate Reservoirs*

Laura Keister[1], Matthew Place[1], Amber Conner[1], David Cole[2], Julia Sheets[2], Susan Welch[2], Kelly Lang[2], Megan Smith[3], and Susan Carroll[3]

Search and Discovery Article #80680 (2019)**
Posted June 10, 2019

*Adapted from poster presentation given at 47th Annual AAPG-SPE Eastern Section Joint Meeting, Pittsburg, Pennsylvania, October 7-11, 2018
 DOI:10.1306/80680Keister2019

[1]Battelle Memorial Institute, Columbus, Ohio (keister@battelle.org)
[2]Lawrence Livermore National Laboratory, Livermore, California
[3]The Ohio State University, Columbus, Ohio

Abstract

The Midwest Regional Carbon Sequestration Partnership (MRCSP) is responsible for the assessment of large-scale carbon dioxide (CO_2) storage associated with enhanced oil recovery (EOR) operations in oilfields that have undergone primary production. As part of this overall program, Battelle has collaborated with The Ohio State University (OSU) and Lawrence Livermore National Laboratory (LLNL) to perform studies investigating potential geochemical reactions caused by the injection of CO_2 and resulting changes to the hydrologic conditions (i.e., porosity and permeability) of the reservoir.

Initially, geochemical equilibrium modeling was performed using analytical data from brine samples collected from the EOR reservoirs. The models indicated that the brines were supersaturated with respect to several carbonate and sulfate minerals prior to the injection of CO_2. The model results also indicate that the saturation levels of these minerals increased with the injection of CO_2. Following the modeling efforts, rock (core) samples collected from the reservoirs were analyzed using scanning electron microscopy-energy dispersive x-ray spectroscopy (SEM-EDX) and powder x-ray diffraction (XRD) to investigate the elemental chemistry and mineralogy of the mineral precipitates present in the large pores and vugs of the core samples. Additionally, stable carbon isotope analyses were performed on the mineral precipitates to assess the origin of the carbon present in the carbonate minerals.

High-resolution micro x-ray computed tomography (XRCT) analysis of core samples collected following the injection of CO_2 was performed to investigate changes in the rock fabric, pore geometry, and fracture conditions resulting from the CO_2 injection. The XRCT scans did not find evidence of mineral dissolution along the fracture surfaces, nor were significant through-going connected fluid pathways observed in any of the core sub-samples. The most compelling evidence for CO_2-induced dissolution was subtle, comprised of localized areas of elevated porosity

within regions displaying similar textures, or slight fracture widening in some cases. In contrast, the evidence of mineral precipitation, lining large pores and even fractures of one sample, was apparent throughout the sub-samples.

Investigation of Potential Geochemical Reactions in Large-Scale Carbon Dioxide-Enhanced Oil Recovery (CO_2-EOR) Carbonate Reservoirs

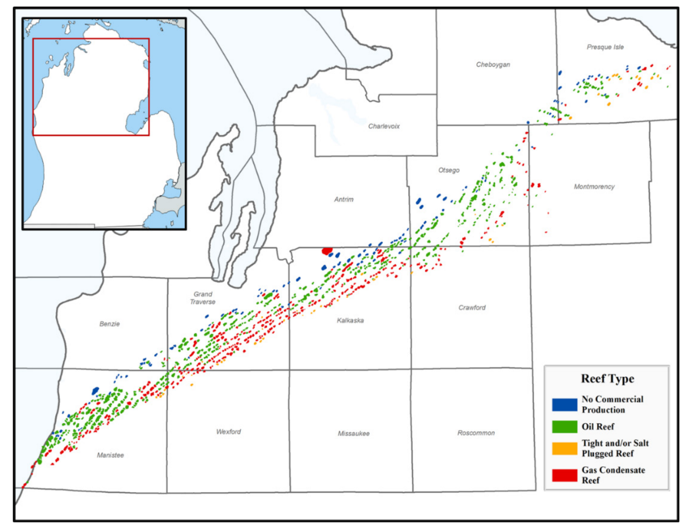
Laura Keister[1], Matthew Place[1], Amber Conner[1], David Cole[2], Julia Sheets[2], Susan Welch[2], Kelly Lang[2], Megan Smith[3], and Susan Carroll[3]
[1]Battelle Memorial Institute, [2]Ohio State University, [3]Lawrence Livermore National Lab

INTRODUCTION

Carbon Dioxide has been injected into the Dover 33 Reef over the past 20+ years as part of EOR operations. During this period, a cumulative 1,555,417 metric tons of CO_2 have been injected. In 2012, MRCSP collected brine and gas samples for geochemical analysis to determine the influence of CO_2 injection on the overall geochemistry of the reef, and whether such changes alter the porosity/permeability. In addition, core samples of the formation were collected in 2016 after injection was complete. Post injection, the core samples were analyzed for $\delta^{13}C$ of carbonates, mineralogy, elemental composition, and microtextural (dissolution/precipitation) features.

GEOLOGIC BACKGROUND

- Reef formed in paleo shallow shelf carbonate depositional system forms circular belt along the margin of the Michigan Basin (Sears, 1979)
- Dover 33 reef is approximately 1 km^2 aerial extent and 100 m in vertical relief
- Reef trend is generally divided in an up-dip direction into gas-, oil-, and water-saturated zones
- Reef height, pay thickness, burial depth, reservoir pressure, and dolomitization varies regionally (Gill, 1979)
- Reservoir facies primarily consist of porous and permeable dolomite with both inter-crystalline porosity and channel porosity.



TECHNICAL APPROACH

Equilibrium models in PHREEQC suggest brines are supersaturated with respect to carbonate, sulfate, and halide minerals – potentially resulting in precipitation.

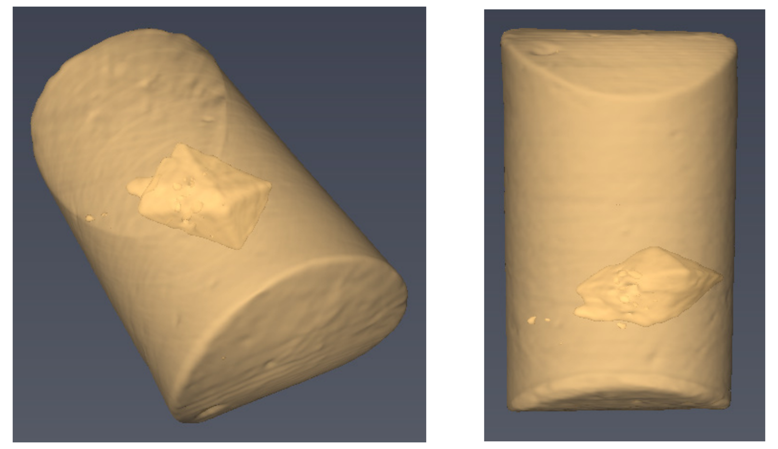
Post-injection core samples from the CO_2-EOR interval are analyzed for evidence of mineral growth (diagenetic v anthropogenic) using light microscopy, XCT, SEM-EDX, XRD, and ^{13}C analyses. Cores were collected after 20 years of CO_2 injection

EQUILIBRIUM GEOCHEMICAL MODELING RESULTS

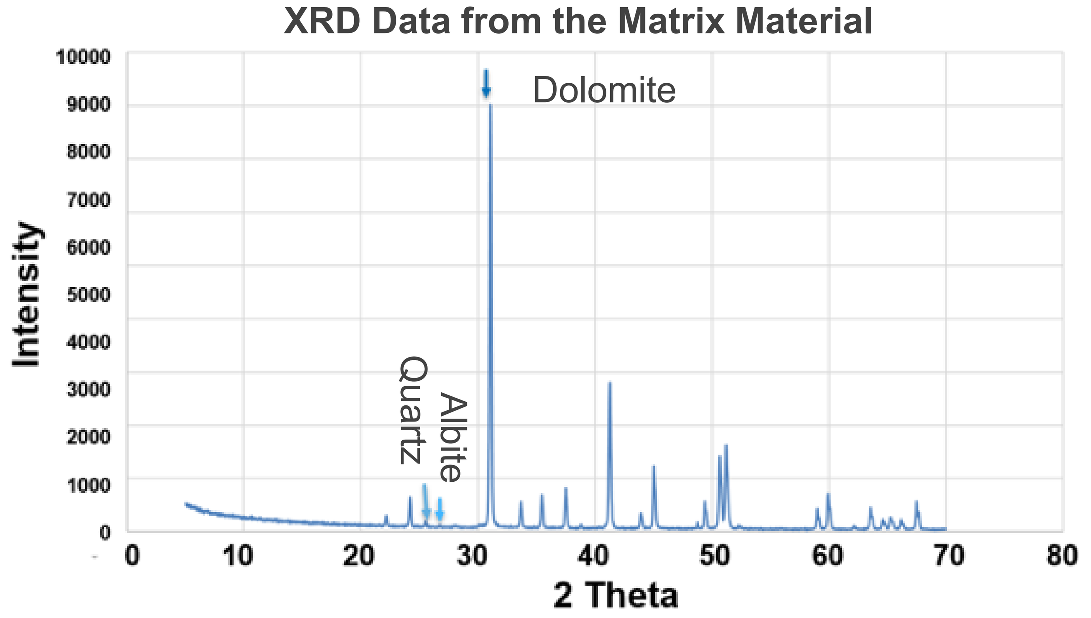
Mineral name	Composition	L-M 1-33 10/11/12	L-M 1-33 10/23/12	L-M 2-33 11/7/12	L-M 5-33 11/14/12
Anhydrite	$CaSO_4$	1.64	1.31	0.99	1.66
Aragonite	$CaCO_3$	3.21	3.40	3.21	3.82
Calcite	$CaCO_3$	3.38	3.57	3.40	3.99
Celestite	$SrSO_4$	2.12	1.74	1.45	2.09
Dolomite	$CaMg(CO3)_2$	6.71	7.08	6.76	7.75
Gypsum	$CaSO_4{:}2H_2O$	0.97	0.81	0.73	1.00
Halite	NaCl	0.72	0.31	0.53	0.62
Sylvite	KCl	-0.08	-0.27	0.06	-0.09

PHREEQC modeling predicts of chemical reactions between the reservoir rock and the injected CO_2 composition. Positive saturation indices suggest precipitation of that mineral is favorable.

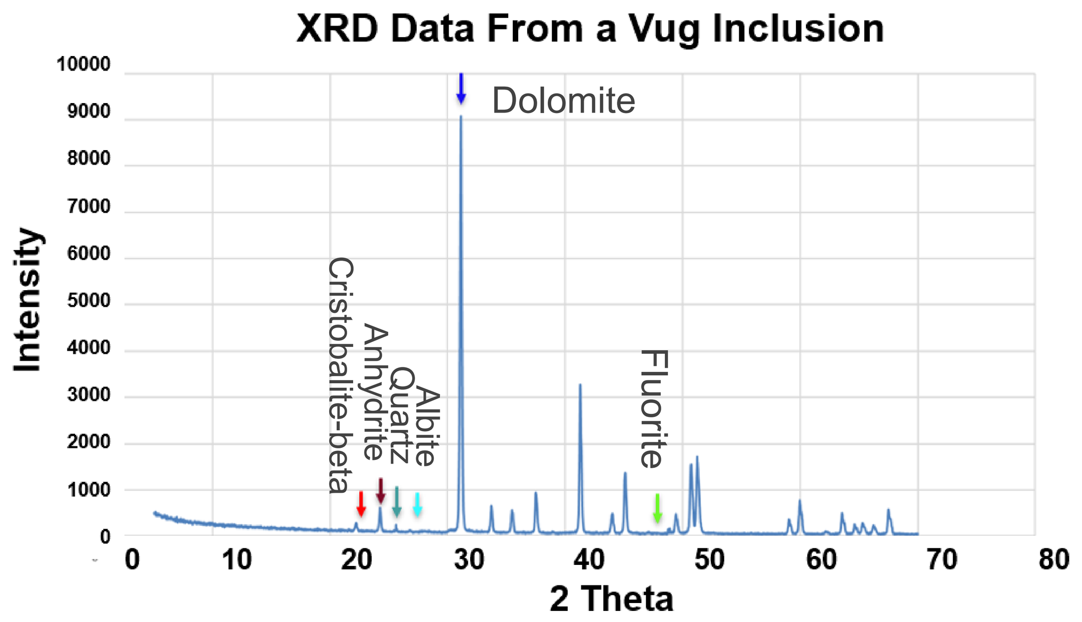
MINERALOGICAL AND LIGHT MICROSCOPY RESULTS



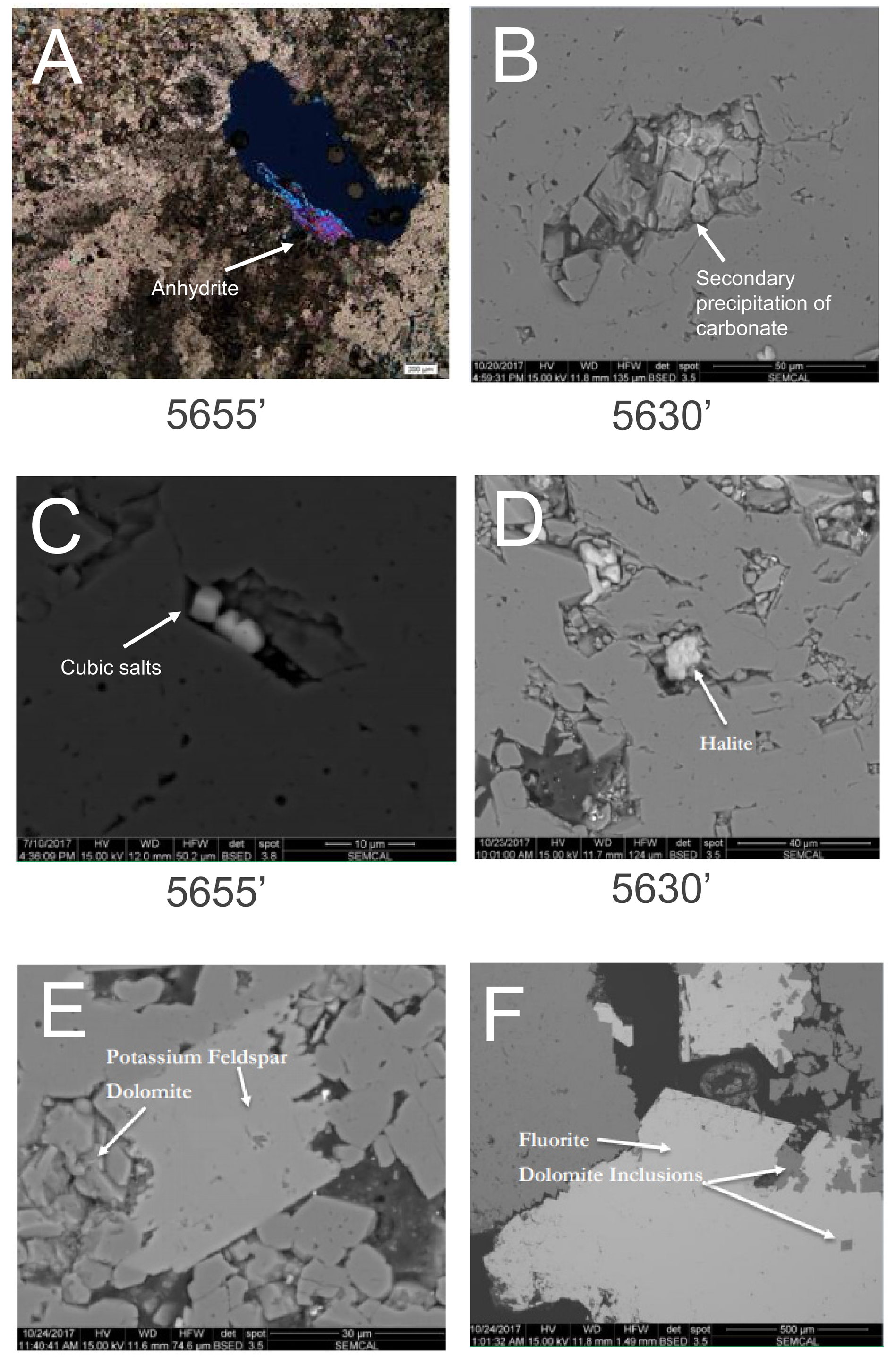
XCT scans of the core (5690.25'), a 3D image of the core and its inclusion was constructed for two different orientations. Aviso software was used to render a 3D image from XCT scans of sample 5690.25', including a partly infilled vug.



Powder XRD analysis show bulk mineralogy of the matrix material. Arrows point to key diffraction maxima that correspond to minerals identified in the core.



XRD analysis shows that, in addition to matrix material (dolomite, quartz, albite), the vug contains anhydrite and fluorite that may have precipitated recently.

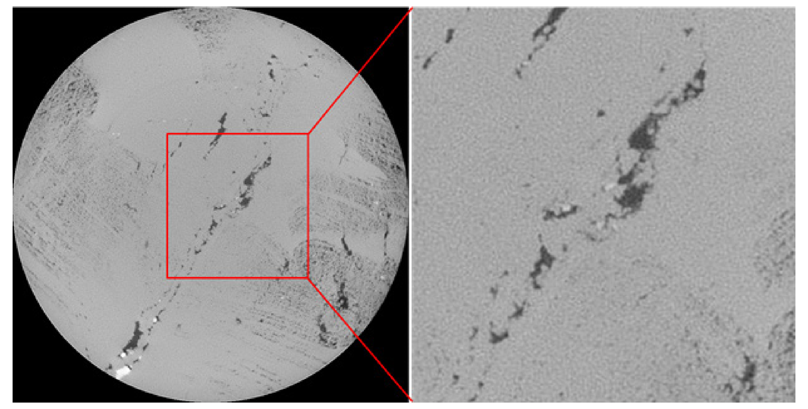


5655' 5630' 5655' 5630' 5588' 5588'

A) Cross polarized light micrograph shows anhydrite precipitation in a vug in the CO_2-EOR interval. B) Backscattered SEM images of carbonate mineral precipitation in a vug in the CO_2-EOR interval. C) and D) SEM imagery shows salts (halite and sylvite) precipitated in vugs in the CO_2-EOR interval. Although these minerals are predicted to precipitate after the injected CO_2 entered the system, they have not been proven to be attributed directly to CO_2-EOR.

E) and F) Backscattered SEM images of potassium feldspar inclusion in a pore space and fluorite inclusion in a pore space. These are examples of minerals detected with XRD that were found in several samples from the CO_2-EOR interval.

μXCT RESULTS



CT images from the CO_2-EOR interval show little textural evidence of dolomite dissolution. These samples do not experience significant smoothing or widening of fracture walls, creation of dissolution channels, rounding of pores, increases in high porosity regions, or through-going connected fluid pathways. LLNL found evidence of mineral precipitation, but was unable to attribute it to diagenesis or CO_2-EOR.

CONCLUSIONS/FUTURE WORK

- The isotopic carbon in the injected CO_2 is heavy (over 20 per mill $\delta^{13}C$) and therefore a potential geochemical tracer. If the carbonates present in vugs and fractures display heavy $\delta^{13}C$ signature, this would provide evidence of precipitation caused by injected CO_2.
- Analyses of vug fillings and carbon isotopes are not conclusive for supporting precipitation of carbonate minerals from the injected CO_2 as predicted by the PHREEQC model. However, slight differences in composition were observed along the rims of some vug carbonates, and isotopic analysis of these materials is ongoing to determine whether such mineralization is isotopically distinct from typical matrix carbonates.
- XRD indicated no difference in carbonate mineralogy between matrix and vug minerals.
- Some XCT analysis of post-injection core suggests that evidence for CO_2-induced dissolution in samples from the CO_2-EOR interval is subtle and difficult to distinguish from diagenesis. It is not clear whether precipitation of calcium sulfate can be attributed to CO_2-EOR, diagenesis, or both.
- The apparent absence of dissolution features and precipitates that are otherwise predicted by the PHREEQC model could be attributed to small sample size, so core imagery is ongoing.

ACKNOWLEDGEMENTS

The study is part of the Midwestern Regional Carbon Sequestration Partnership (MRCSP) Michigan Basin Large-Scale Injection Project, which is part of a larger national carbon storage research program headed by the United States Department of Energy. The MRCSP (www.MRCSP.org) is funded under DOE/NETL Cooperative Agreement # DE-FC26-0NT42589 with co-funding by Core Energy, LLC, and other partners.