

Effect of CO₂-Brine-Rock Reactions on Pore Architecture and Permeability in Dolostone: Implications for CO₂ storage and EOR

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Abstract

Geologic carbon sequestration (GCS) is considered a feasible technology for storing substantive volumes of greenhouse gases in subsurface geological formations. In the reservoir, far from carbon dioxide (CO₂) injection wells or in post-injection scenarios, diffusion dominates over advection. This condition conjoins with spatially distributed geochemical reactions to induce heterogeneous changes in pore architecture, i.e. pore body and throat sizes or surface roughness. These changes can affect CO₂ transport properties and storage capacity. In this work, we investigated mineral dissolution and precipitation in dolomite samples saturated with a CO₂-saturated brine at 93 °C and 34.5 MPa, aged without flow. Two rock types samples, i.e. intergranular- and

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vuggy-dominant, were selected to investigate changes in pore size, porosity and permeability under reactive conditions. Mineral dissolution and precipitation were characterized using scanning electron microscopy. Changes in pore size were quantified via Time-Domain Nuclear Magnetic resonance (TD-NMR) transverse relaxation time (T_2) and diffusion coefficient (D) distributions. We show that mineral dissolution likely occurs in highly permeable pathways. These observations are confirmed through analysis of (T_2) and diffusion coefficient (D) distributions. In contrast to results during CO_2 -enriched brine continuous injection, mineral precipitation was observed in micropores. The leftward shift of the T_2 peaks, corresponding to micropores, also evidenced mineral precipitation in low-permeability zones. However, microscale alterations resulted only in a subtle increase in porosity and permeability. Results in this study shed light on effects of geochemical reactions on alteration of rock properties in diffusion-dominated regions during CO_2 storage.

Keywords: CO_2 storage, Heterogeneous geochemical reactions, Pore structure change, Porosity and permeability change, NMR T_2 and diffusion

1. Introduction

Carbon dioxide (CO_2) emissions from the energy sector powered by fossil fuels have noticeably increased CO_2 concentration in the atmosphere, which has been touted as a significant contributing factor to climate change (Hofert et al., 2002; Bachu, 2000). Mitigation strategies have been proposed to reduce emissions substantively through safe injection of CO_2 into subsurface reservoirs such as deep saline aquifers (Van der Meer, 1995; Bachu, 2003;

8 Steele-MacInnis et al., 2012; Liu et al., 2016; Trevisan et al., 2017; Wang et al.,
9 2020), depleted oil/gas reservoirs (Li et al., 2006; Han and McPherson, 2009;
10 Wang et al., 2013; Sun et al., 2016; Olalotiti-Lawal et al., 2019), unminable
11 coal beds (Gale and Freund, 2001; Stauffer et al., 2011; Cao et al., 2020) and
12 oil/gas reservoirs (Shaw and Bachu, 2002; Dai et al., 2013; Tao and Clarens,
13 2013; Wang et al., 2014; Gong and Gu, 2015; Yu et al., 2020). This strategy
14 is denominated geologic carbon storage (GCS). Among GCS targets, deep
15 carbonate saline aquifers are ideal candidates due to their broad geographical
16 distribution, large storage capacity, and potential long-term storage security
17 (Bruant et al., 2002; Friedmann, 2007; Benson and Cole, 2008). However,
18 carbonate reservoirs are reactive in the presence of CO_2 in the brine. CO_2
19 dissolution in brine leads to a pH decrease (Kaszuba et al., 2005). In view of
20 the pH drop, understanding of mineral dissolution and precipitation, and the
21 associated changes in static and dynamic properties of rocks, are important
22 considerations for GCS operations.

23 The impacts of geochemical reactions on pore architecture and petro-
24 physical properties are complex, and they relate to chemical, physical and
25 geological characteristics, such as fluid composition, temperature, pressure,
26 mineralogy and transport properties. In addition, mineral dissolution and
27 precipitation are strongly dependent on the coupling between the local fluid
28 transport and the distribution of dissolved ions. The fate of CO_2 directly
29 relates to the interplay between geochemical reactions and the transport of
30 species within CO_2 -enriched formation brine. Of equal importance are the
31 spatial heterogeneity of the pore geometry as well as mineral distribution
32 that result in heterogeneity of the mineral dissolution and precipitation. At

33 the pore-scale, reactions along mineral boundaries and different associated
 34 reaction mechanisms in pores of different sizes, and consequently different
 35 surface-to-volume ratios, enable heterogeneous changes in pore structure and
 36 properties along flow pathways (Tenthorey and Scholz, 2002; Noiriel et al.,
 37 2016; Min et al., 2016; Beckingham, 2017; Luhmann et al., 2017; Adeoye
 38 et al., 2017; Noiriel and Deng, 2018). Moreover, changes in fluid composition
 39 after reactions in the pore space can give rise to Gibbs free energy gradients,
 40 potentially increasing the contrasts in mineral reactivity at various locations,
 41 such as pore throats between micro and macropores. Heterogeneous distri-
 42 butions of mineral dissolution and precipitation in the pore space ultimately
 43 contribute to changes in pore architecture, i.e. pore shape, pore-size distri-
 44 bution, and mineral reactive surface area. The complex interplay may either
 45 widen or clog pores to ultimately impact static and dynamic rock properties,
 46 such as porosity, permeability and wettability (Luquot and Gouze, 2009; Sad-
 47 hukhan et al., 2012; Nogues et al., 2013; Chen et al., 2014; Luhmann et al.,
 48 2017; Yee et al., 2018).

49 Current GCS research using laboratory experiments focuses on investigat-
 50 ing changes in porosity and permeability in convective-dominant regions by
 51 continuously injecting CO₂-enriched brine, which typically leads to uniform
 52 dissolution as the porous medium is surface-reaction controlled (El-Maghraby
 53 and Blunt, 2012; Adeoye et al., 2017). For instance, Luquot and Gouze (2009)
 54 studied porosity and permeability changes in four zones corresponding to
 55 increasing distances from the injection well; these dissolution experiments
 56 showed power-law scaling, $k \sim \phi^n$, between permeability and porosity with
 57 different values of the n scaling exponents. Regardless of differences in field

58 injection practices, reservoir regions with convective-dominated transport as
 59 well as those with negligible convection arise. As CO₂ injection is interrupted,
 60 the convective flow is stopped and transport becomes a rate-limiting process.
 61 In this case, reactions are diffusion-dominated. Mass transport between the
 62 mineral surface and the pore center, or between micro and macropore spaces
 63 are limited, thus leading to poor mixing conditions (Molins, 2015). Heteroge-
 64 neous pore-scale architecture favors the buildup of the aforementioned local
 65 chemical concentration gradients. Overall, localized dissolution and precipi-
 66 tation events occur under these conditions, thus potentially increasing or
 67 decreasing the conductivity of specific flow pathways, which in turn drive
 68 changes in permeability (Kang et al., 2010). To date, very few research ef-
 69 forts focus on diffusion-dominant zones (shown in Figure 1) and subsequent
 70 consequences of limited supply of carbonic acid on petrophysical properties.

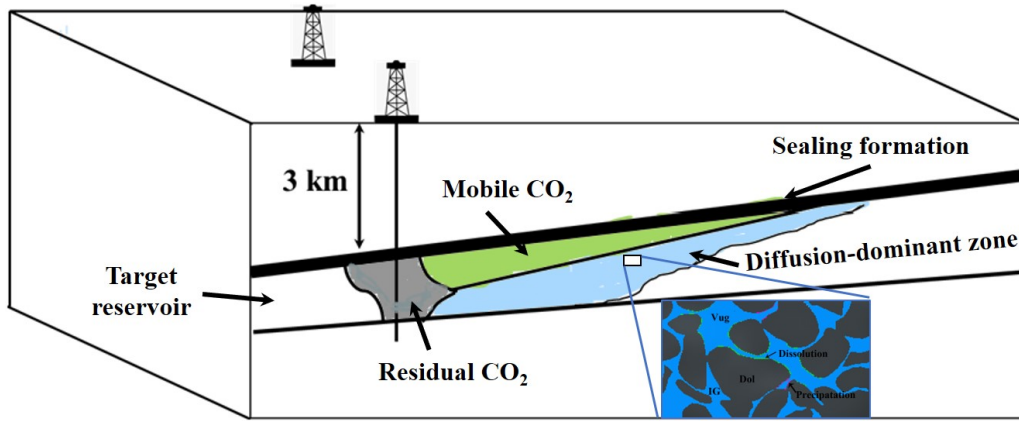


Figure 1: Schematic diagram of CCS/EOR scenario in a subsurface target reservoir. For regions far from injection wells or in post-injection periods, diffusion dominates over advection.

71 The objective of this study is to investigate complex changes in pore ar-

72 chitecture, i.e. pore body and pore throat sizes, or surface roughness, and
73 petrophysical properties (i.e. porosity and permeability) caused by the het-
74 erogeneous geochemical reactions in the pore space in regions far from carbon
75 dioxide (CO_2) injection wells or during post-injection scenarios. Dolomite
76 samples were collected from the two rock types identified, namely vuggy-
77 and intergranular-dominant porosity in the Madison Limestone, which is lo-
78 cated in the Rock Springs Uplift (RSU), Southwestern Wyoming (shown in
79 Figure 2) (Surdam, 2013; Wang et al., 2018). In this research, we investigated
80 changes in pore architecture and their impact on permeability and porosity
81 in two different rock types as driven by mineral dissolution and precipitation
82 in a diffusion-dominated system containing limited carbonic acid. To mimic
83 this condition, the core samples were reacted with stagnant CO_2 -enriched
84 brine in a core-flooding apparatus at reservoir conditions (34.5 MPa and 93
85 $^{\circ}\text{C}$) for 400 hours. Our results uncover connections between reactivity in
86 diffusion-dominant regions and potential large-scale effects on storage, as to
87 provide a better understanding of the subsequent dynamics of the multiphase
88 flow system.

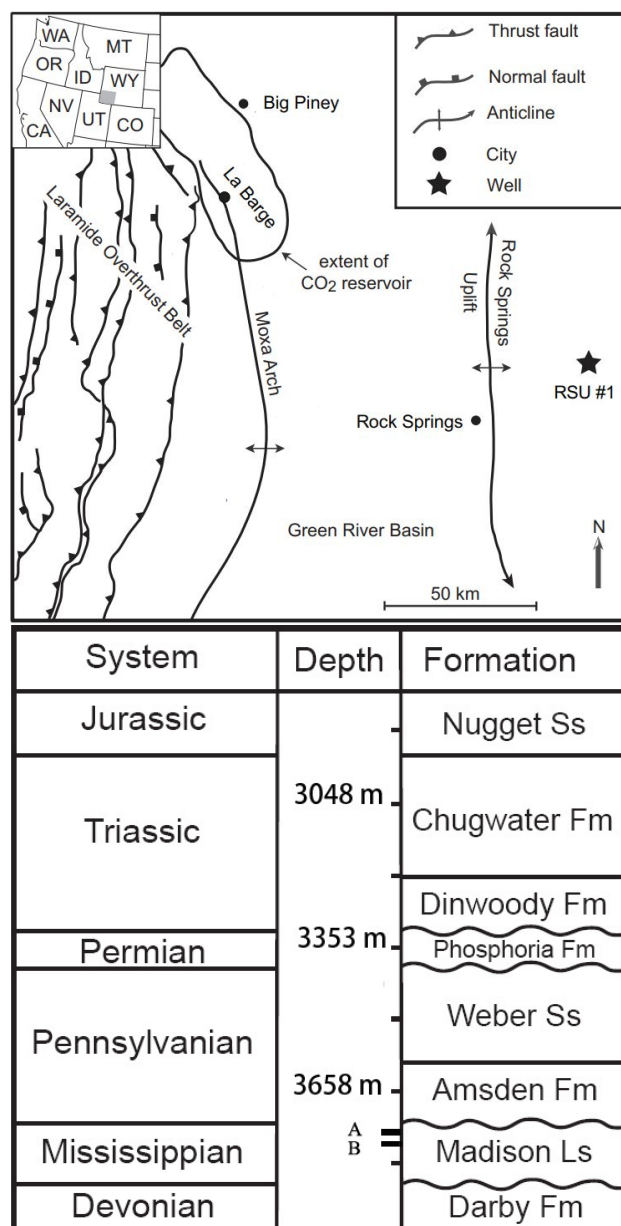


Figure 2: Top: Geologic map of Rock Springs Uplift, Southwestern Wyoming, United States, and the location of well RSU #1 where the rock samples were drawn. RSU = Rock Springs Uplift.; Bottom: Stratigraphic column for well Rock Springs Uplift #1 including cored intervals: Madison samples were collected from depth interval A (3766 m) and B (3783 m). Fm = formation; Ss = Sandstone; Ls = Limestone.

89 2. Experimental Section

90 2.1. Materials

91 Brine used in the experiments was prepared based on the chemical com-
92 position of the formation brine in the Madison Limestone, as shown in Ta-
93 ble 1. The brine was degassed for four hours under vacuum before use in the
94 experiment. A second, CO₂-saturated brine was prepared by equilibrating
95 degassed synthetic brine with CO₂ (99.999% purity) for 24 hours at reservoir
96 conditions (34.5 MPa and 93°C).

97 Four core plugs (24.3 mm in diameter and 50.0 mm in length) of Madison
98 Limestone recovered from the well RSU#1 were selected for experiments.
99 Two of the four samples (MH1 and MH3) are dominated by vuggy pores
100 and two additional samples (MH2 and MH4) are dominated by intergran-
101 ular pores (Table 2). All four samples were cleaned in soxhlet extractors
102 using toluene and methanol, and oven-dried at 100°C for 24 hours. Routine
103 core analyses (nitrogen porosity and permeability) were carried out under
104 a net confining pressure of 3.5 MPa using a Coreval 700 permeameter and
105 porosimeter (VINCI Technologies, France). Klinkenberg permeabilities of the
106 core plugs were used to correct nitrogen permeability measured to equivalent
107 liquid permeability. Properties of each sample are summarized in Table 2.
108 Samples prepared for the scanning electron microscope (SEM) and thin sec-
109 tion were trimmed from these core plugs. Two addition samples (mini plugs
110 MH5 and MH6: 8 mm in diameter and 10 mm in length) were drilled near
111 the extraction locations of samples MH3 and MH4 for diffusion coefficient
112 measurements.

Table 1: Chemical concentrations of synthesized and produced brine. pH of the degassed synthetic brine is 6.7.

Major Species/Complexes	Concentration, mol/kg
SO4	0.1052
Cl	1.6190
Na	1.4760
K	0.0596
Mg	0.0030
Ca	0.0040

Table 2: Core plug properties before and after reaction. The standard errors of the nitrogen porosity and Klinkenberg permeability are $\pm 0.05\%$ and ± 0.5 mD, respectively

Pore-type	Sample #	Depth, m	Porosity, %		Permeability, mD	
			before	after	before	after
Intergranular	MH1	3765.8	16.22	16.39	14.06	15.27
	MH3	3765.9	19.46	19.66	14.21	16.91
	MH5	3765.9	-	-	-	-
Vuggy	MH2	3782.6	18.16	19.45	65.09	74.90
	MH4	3782.7	16.34	17.26	30.76	40.67
	MH6	3782.7	-	-	-	-

113 *2.2. SEM and Thin Section*

114 Core plugs MH1 and MH2 were evaluated using thin section and scanning
115 electron microscope (SEM) analyses to characterize mineralogy and pore ar-
116 chitecture and to identify potential mineral dissolution and precipitation.
117 Selected samples were sent to Wagner Petrographic, Lindon, Utah, for thin
118 section preparation. Most of the thin sections were stained for calcite and
119 ferroan carbonates, and impregnated with epoxy for porosity evaluation. SEM
120 analysis was performed using an FEI Quanta FEG 450 field emission scan-
121 ning electron microscope. Samples were carbon-coated for high-vacuum SEM
122 analysis ($> 10^{-5}$ torr) and backscattered electron images were obtained using
123 a 20 kV electron beam.

124 *2.3. Transverse Relaxation Time (T_2)*

125 ^1H NMR T_2 relaxation time, also known as transverse relaxation time, can
126 be used to estimate pore-size distribution. For rock samples fully saturated
127 with brine, proton spins relax through three independent relaxation mecha-
128 nisms: bulk fluid ($T_{2, \text{bulk}}$), surface ($T_{2, \text{surface}}$) and diffusion ($T_{2, \text{diffusion}}$). In
129 the fast diffusion regime, the T_2 relaxation can be calculated as (Wang et al.,
130 2018):

$$\frac{1}{T_2} = \frac{1}{T_{2, \text{bulk}}} + \frac{1}{T_{2, \text{surface}}} + \frac{1}{T_{2, \text{diffusion}}} \quad (1)$$

131 As diffusion relaxation is minimized and bulk relaxation rate is sufficiently
132 small, T_2 is dominated by $T_{2, \text{surface}}$. T_2 can then be simplified as (Wang et al.,
133 2018):

$$\frac{1}{T_2} \approx \rho \frac{S}{V_p} \quad (2)$$

where ρ is surface relaxivity; S and V_p are surface area and pore volume, respectively. As the V_p/S ratio is proportional to pore size, the T_2 distribution relates to the pore-size distribution.

The area under the T_2 distribution curve is proportional to the number of hydrogen protons that are contained in the pore fluids within the sensitive volume. The division between different pore sizes using fixed cutoff values is commonly used to separate the bound and free fluid portion in NMR data interpretations. Figure 3 shows an example of T_2 distribution of a core plug (porosity is ϕ) fully saturated with brine. The shortest T_2 represents fluid (A1) that is bounded by clay. The smaller pores, also known as micropores (faster T_2), contain capillary fluid (A2) that is bound by capillary forces and the remaining water film in larger pore surfaces. The largest pores, also known as macropores (the largest T_2), contain free fluid (A3) or fluid that is free to move. The porosity of the larger pores can be calculated as $\phi A3/A$. This method will be used to investigate the change in pore size or its corresponding porosity induced by the mineral dissolution and precipitation. In this study, NMR T_2 measurements of samples MH3 and MH4 before and after reaction were collected using a Bruker BioSpin LF110 instrument at 25°C and atmospheric pressure using a standard Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence.

2.4. Restricted Diffusion Coefficient

The effective diffusion coefficient measured using pulsed field gradient (PFG) NMR has been used to provide a better understanding of fluid trans-

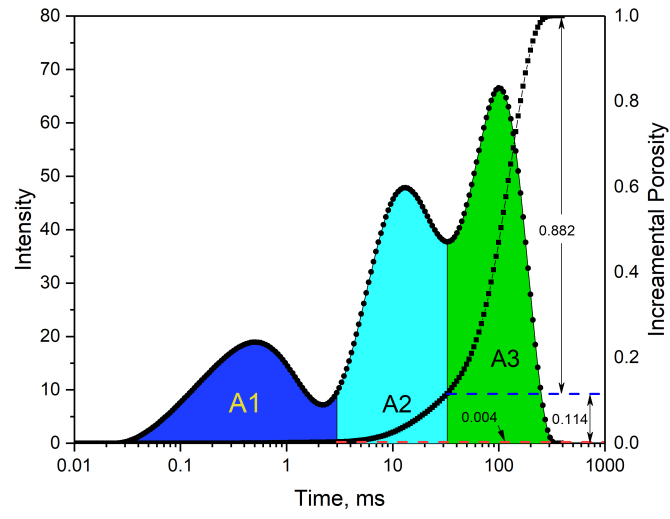


Figure 3: An example of T_2 distribution of a core plug saturated with brine. The porosity of different pore types divided by two cutoff values can be expressed as A_i/A , where A_i is A_1 , A_2 and A_3 .

157 port in diffusion-dominant regions and to provide the effective diffusion co-
 158 efficient spectra (Wang et al., 2018). In the short observation time limit,
 159 the root-mean-squared displacement for a fraction of the diffusive water
 160 molecules near pore surfaces is reduced compared to the value of the bulk
 161 fluid free diffusion. In porous media, hydrogen-bearing molecules exist in a
 162 variety of different pore sizes, where the measured signal attenuation is a sum
 163 of contributions from all hydrogen spins. As a result of the gradient increase,
 164 a deviation of the logarithm of intensity ratio will occur. A non-negative
 165 least-square algorithm can be used to fit the diffusion coefficient decay curve
 166 and to calculate diffusion coefficient distribution (Wang et al. (2018)). The
 167 calculated diffusion coefficient distribution not only represents pore-size dis-
 168 tribution, but it also provides a hint of molecular diffusive transport in pores
 169 of different sizes. In this study, the two mini plugs (MH5 and MH6) were
 170 reacted with CO₂-saturated brine inside a transfer vessel at reservoir condi-
 171 tions. NMR diffusion coefficients before and after reaction were determined
 172 at a series of gradient strengths to quantify the changes in spatial diffusion
 173 coefficient distribution. The diffusion coefficient for the mini plugs were col-
 174 lected using a Bruker BioSpin mq20 instrument with a 10 mm (diameter)
 175 × 10 mm (length) chamber. The pulsed field gradient NMR sequence in-
 176 troduced by Stejskal and Tanner (1965) was selected. In the fast-diffusion
 177 regime, the spin echo amplitude is described as:

$$\ln \frac{I(g)}{I(0)} = -\gamma^2 g^2 \delta^2 D \left(\Delta - \frac{\delta}{3} \right) \quad (3)$$

178 where δ is the length of a gradient pulse, γ is the proton gyromagnetic ratio,
 179 g is the applied gradient strength, and $I(g)$ and $I(0)$ are the amplitude of the

180 signal after the first radio frequency pulse with and without gradient strength
181 being applied, respectively. The amplitudes of the gradients strengths range
182 from 2.17 to 3.29 T/m, with a total of 30 points collected. Since the diffusion
183 coefficient is sensitive to temperature, a fluid circulator (F12-MA, JULABO
184 USA Inc.) with a temperature accuracy better than ± 0.02 °C was used to
185 warm the sample by circulating temperature-constant coolant liquid.

186 *2.5. Geochemical Reaction Experiment*

187 Geochemical reaction experiments were conducted in a high pressure/high
188 temperature core-flooding system, as shown in Figure 4. Core plugs were
189 wrapped with a heat-shrink tube and Viton sleeve before placing them in a
190 coreholder. Synthetic brine was added to fully saturate the core plugs at the
191 start. Upon saturation, the samples were brought up to reservoir conditions
192 (34.5 MPa and 93 °C). High precision syringe pumps (260D, Teledyne ISCO)
193 were used to inject fluids and to maintain the confining and back pressures
194 (pore pressure). Core plugs were first equilibrated with brine at reservoir
195 conditions for 400 hours. CO₂-saturated brine was then injected into the
196 core plug to fully displace the synthetic brine. The core-flooding system was
197 subsequently shut in and the core plug reacted with CO₂-saturated brine for
198 an additional 400 hours.

199 As the experiment was finished, the core plugs were flushed with 10 pore
200 volumes of deionized water to displace the brine to prevent subsequent salt
201 precipitation. Then, they were further cleaned in soxhlet extractors using
202 toluene and methanol, and oven-dried at 100 °C for 24 hours. The cleaned dry
203 core plugs were used for additional measurement, i.e. gas (N₂) permeability,
204 porosity, and NMR-T₂ distribution to detect potential changes after reaction.

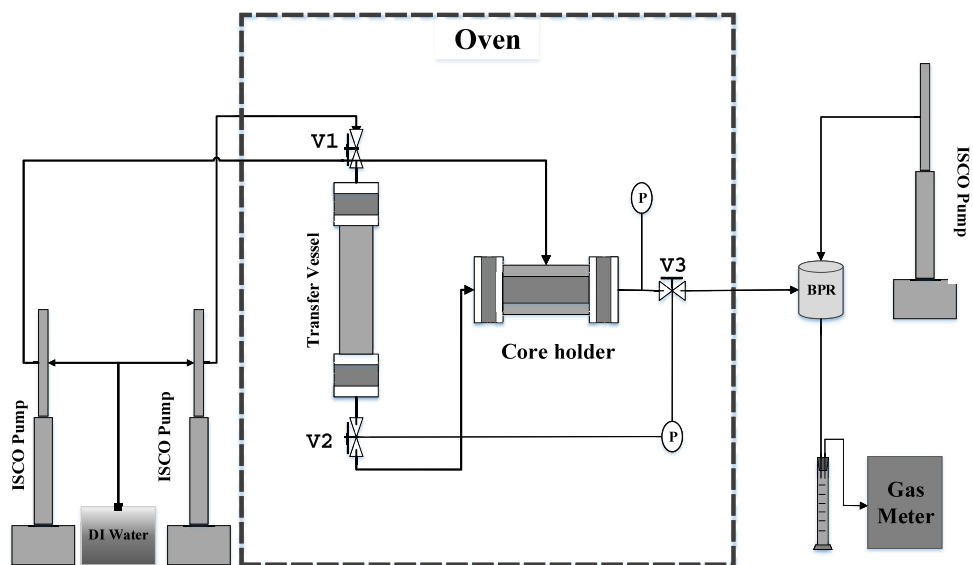


Figure 4: Schematic of coreflooding system used in this study. Once a constant gas production rate is monitored by the gas meter, valves V2 and V3 are closed for stagnant reaction purpose.

205 Finally, samples were collected from the samples MH1 and MH2 for SEM
206 imaging to detect potential mineral dissolution and precipitation.

207 **3. Experimental Results and Discussion**

208 *3.1. Influence of Geochemical Reactions on Porosity and Permeability*

209 The Madison Limestone rock samples exhibit two styles of porosity, namely
210 intergranular-dominant, characterized by a homogeneous pore-size distribu-
211 tion, and vuggy-dominant, characterized by a variable pore-size distribution
212 (McLaughlin et al., 2012, 2013). Examples of the porosity types are shown
213 in Figure 5a. The figure shows a vug that is surrounded by smaller, uni-
214 form dolomite grains that typify the reservoir’s intergranular porosity system.
215 Though the intergranular pores are smaller, they are evenly distributed and
216 provide the majority of the pore space. For vuggy-dominant pores, vuggy,
217 sometimes moldic, porosity forms by diagenetic dissolution of the carbonate
218 and/or anhydrite (Figure 5b). In addition, small secondary mineral particles
219 of quartz and dolomite up to 10 μm were observed on the surface of primary
220 dolomite and quartz grains.

221 CO_2 -brine-rock reactions can induce mineral dissolution and precipita-
222 tion to lead to changes in porosity by widening or clogging pore-bodies and
223 pore-throats. Mineral dissolution increases pore volume while precipitation
224 does the opposite. The net change of porosity is determined by the balance
225 between these mechanisms. In this study porosity measured before and after
226 reaction are provided in Table 2. The increments in porosity for MH1 and
227 MH3 (intergranular-dominant samples) are 0.17% and 0.2%, respectively.
228 The small difference mainly results from the finite amount of carbonic acid

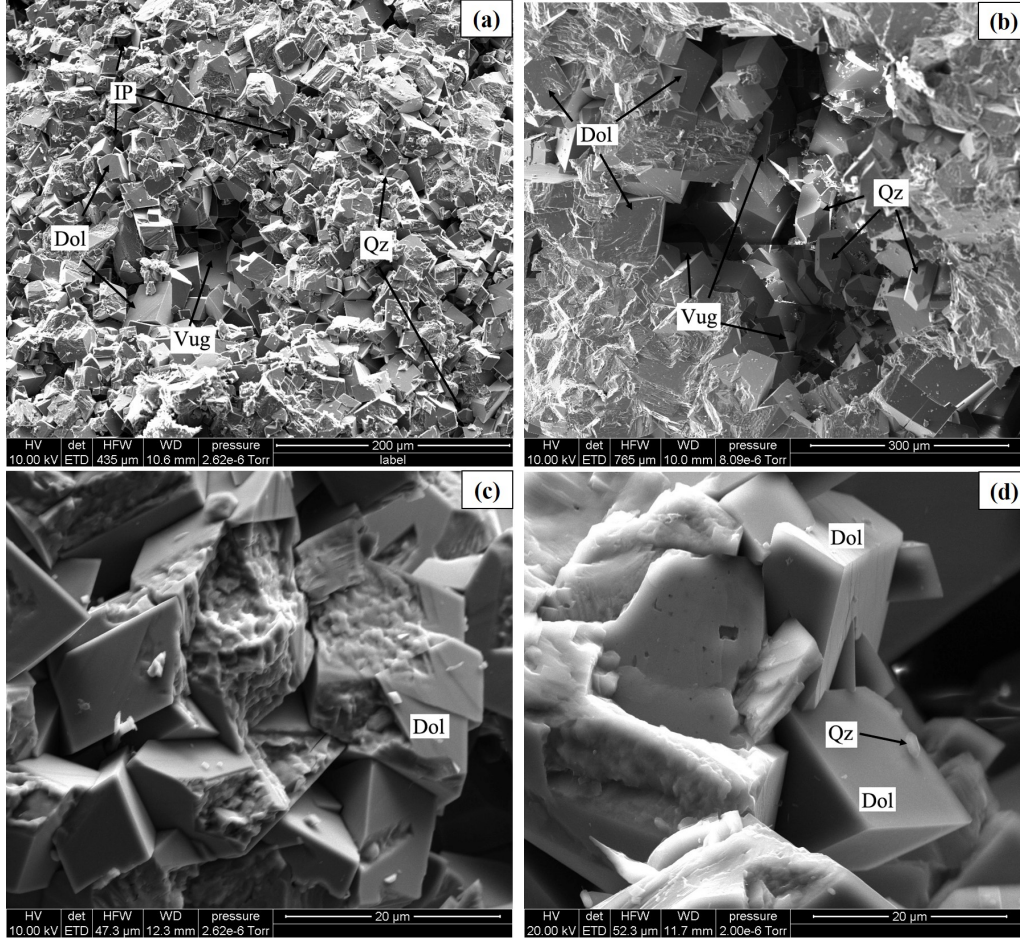


Figure 5: Scanning electron microscope (SEM) of samples MH1 and MH2 prior (a and b) and after (c and d) reaction. (a) MH1: a mixed intergranular and vuggy porosity system. (b) MH2: a dominantly vuggy porosity system. Authigenic quartz crystals have nucleated in vugs. (c) MH1: pitting on the crystal surface and broken crystal faces becomes deeper. (d) MH2: pitting on the crystal surfaces became deeper and small particles on the surface of dolomite crystals are mostly dissolved. Dolomite crystals around vuggy pores become smaller than matrix dolomite grains. Dol: dolomite; Anh: anhydrite; Qz: quartz; IP: intergranular pore.

229 in the brine and slow reactive-diffusive transport when in contact with the
230 acid brine in the reaction process. As opposed to intergranular-dominant
231 samples, the porosity of vuggy-dominant samples, MH2 and MH4, increased
232 from 18.16 to 19.45% and from 16.34 to 17.26%, respectively. In addition
233 to the chemical reactions, the physical loss of grains and the movement of
234 clay, or dolomite and quartz fine particles might also contribute to the in-
235 creasing porosity in both samples (Pearce et al., 2016; Dávila et al., 2017;
236 Pearce et al., 2019). Pearce et al. (2019) observed that the changes in poros-
237 ity calculated from μ CT density is less than 0.5% owing to movement of
238 clays or fines. However, McLaughlin et al. (2012) showed that the Madison
239 Limestone contains minor clays and fine particles, which can also be found in
240 the SEM images before the reaction in Figure 5. Therefore, compared with
241 chemical reactions, the porosity increased due to the physical movement of
242 the clays and fine particles is relatively negligible.

243 Porosity of sample MH1 is comprised mainly of homogeneous intergran-
244 ular pores. These pores were filled by CO₂-saturated brine and pore walls
245 dissolved uniformly. Negligible dissolution of dolomite occurred (Figure 5
246 (c)), because of the limited volume of reactive fluids. However, etch pits on
247 mineral surfaces suggest dolomite dissolution. The most prominent dissolu-
248 tion texture within the intergranular sample are nascent channel structures
249 with walls of smaller (relative to matrix), partially digested dolomite crystals.

250 Figure 5 (d) shows an SEM image highlighting vuggy pores. The small
251 mineral particles (dolomite) on the surface of dolomite crystals are mostly
252 dissolved. Pitting of crystal surfaces became deeper after reactions, while dis-
253 solution on the edge and corner of dolomite crystals cannot be validated based

254 solely on the SEM images. Pore systems in sample MH2 are vug-dominated.
255 The displacing reactant fluid mainly flowed along the most highly permeable
256 pathways, suggesting dissolution reactions happen, while in surrounding in-
257 tergranular pores (matrix), the reactions are limited (Luquot et al., 2014).
258 In addition to the mineral dissolution, mineral precipitation is also observed
259 in both rock samples, shown in Figures 6 and 7. The newly precipitated
260 minerals are located on dolomite crystals in micropores and have a distinctly
261 irregular morphology. The energy dispersive spectra (EDS) of neoformed
262 minerals from two post-reacted samples and from pre-reacted dolomite crys-
263 tals were collected within red circled area, shown in Figures 6 and 7. Ele-
264 ments such as Ca, C, O, Mg are shown in the EDS spectra of both original
265 dolomite and the neoformed minerals, indicating that the precipitated min-
266 erals are chemically similar to the originally present. However, it is hard to
267 determine whether the precipitates are dolomite or a mixture of dolomite
268 and calcite solely from the EDS spectra.

269 In contrast with changes in porosity after geochemical reactions, perme-
270 ability evolves non-linearly, which is likely driven by the spatial distribution
271 of reactions in individual pores and pore-throats. In this study, permeability
272 for MH1 and MH3 increased from 14.06 and 14.21 mD to 15.27 and 16.91
273 mD, respectively. Mineral dissolution, as observed from SEM images shown
274 in Figure 5, increased the smoothness of pore surface, widening the pore
275 body and pore throat along the flow pathways, thus increasing permeability
276 after reaction. Even though porosity of MH1 and MH3 is similar to that of
277 MH2 and MH4, it is somewhat surprising that permeability after reactions
278 increased 1.2 and 1.3 times, respectively, for the latter samples. The incre-

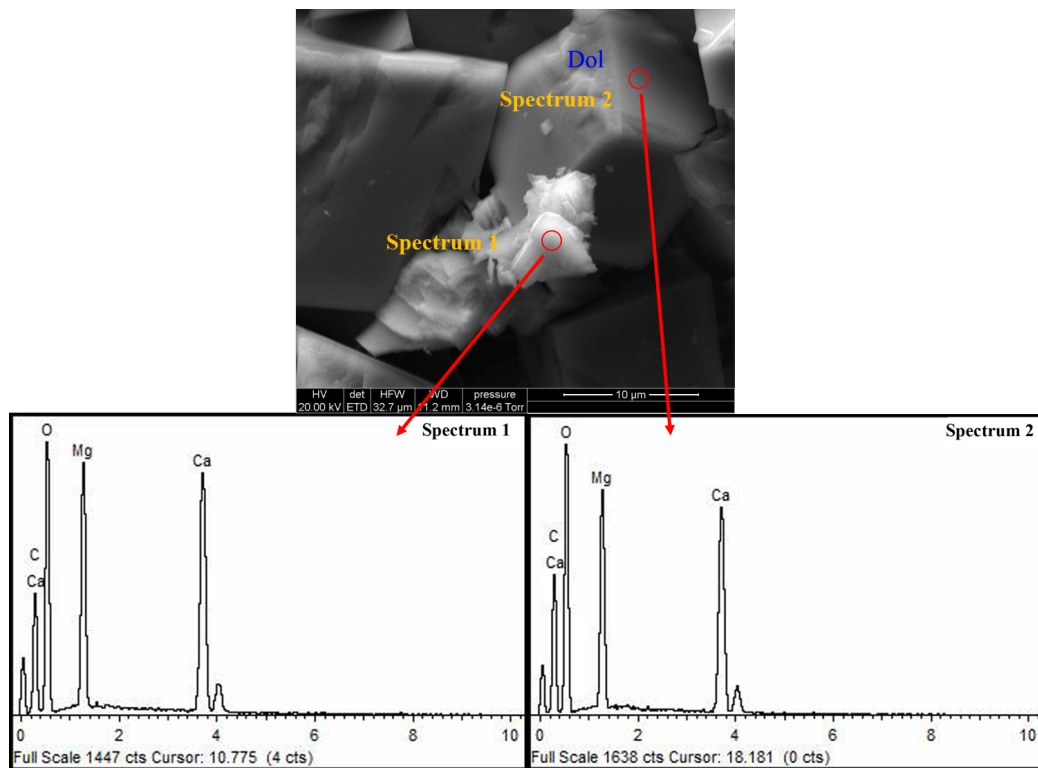


Figure 6: SEM image and EDS spectra (within red circles) of originally and newly precipitated mineral in sample MH1. Comparison of Spectrum 1 (neoformed mineral) to host dolomite(Spectrum 2) shows that the newly precipitated minerals are chemically similar to original dolomite. Dol: dolomite.

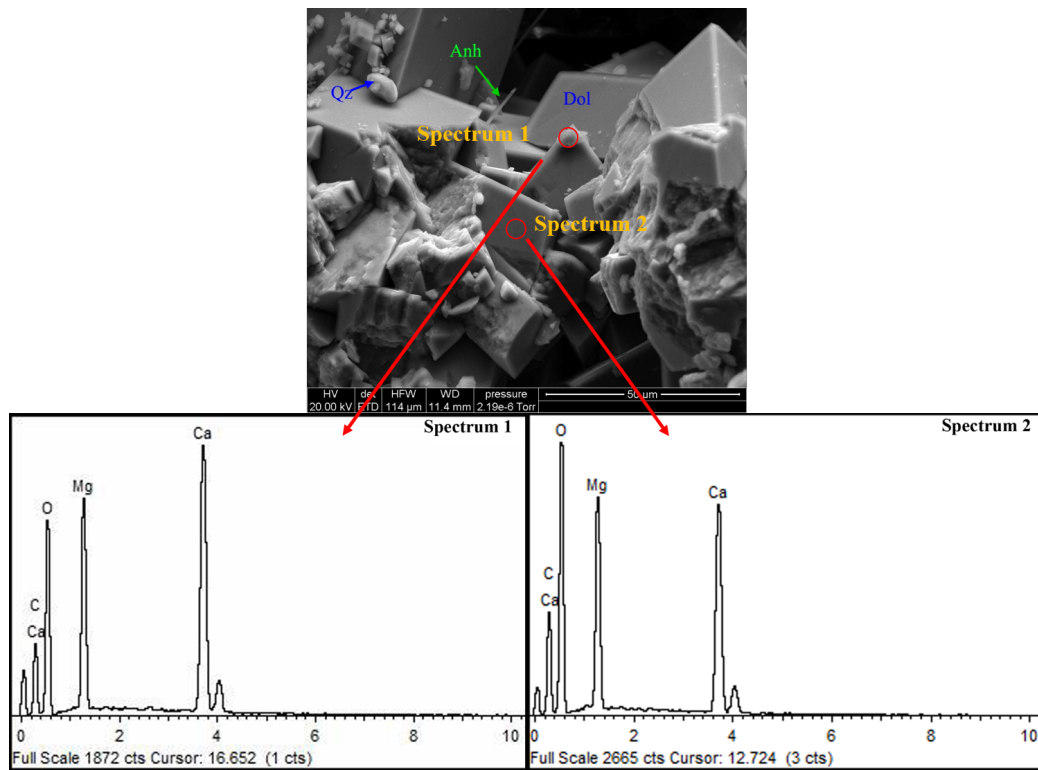


Figure 7: SEM image and EDS spectra (within red circles) of originally and newly precipitated minerals in sample MH2. Comparison of Spectrum 1 (neoformed mineral) to host dolomite (Spectrum 2) show that the newly precipitated minerals are chemically similar to original dolomite. Dol: dolomite; Qz: quartz; Anh: anhydrite.

279 ment of permeability are likely induced predominantly by pore-throat size
280 alteration, especially for the smaller pore throats along the flow pathways
281 (Luhmann et al., 2017). Irreversible geochemical changes may occur, such
282 as creating new flow pathways, which has a significant influence on perme-
283 ability (Rutqvist, 2012). The changes in pore size that mostly relates to
284 pore-throat size can be recorded from the NMR T_2 and effective diffusion
285 coefficient distributions, which will be discussed in the following sections.

286 3.2. NMR T_2 Distribution

287 Pore size changes due to mineral dissolution and precipitation can be de-
288 termined from T_2 distributions of hydrogen nuclei, in which the longer T_2
289 values correspond to smaller surface area-to-volume ratio, thus larger pores.
290 The transverse relaxation for the two type samples shows different responses.
291 In Figure 8 (A), two peaks with a shorter T_2 peak and a longer T_2 peak are
292 shown in the T_2 distribution of MH3, representing micro and intergranular
293 pores, respectively. As the porosity of sample MH3 is dominated by inter-
294 granular pores, the area under the longer T_2 peak is much larger compared to
295 the porosity of micropores. The T_2 of the rightmost peak that corresponds
296 to larger intergranular pores increases from 65.3 to 67.1 ms after reaction,
297 suggesting mineral dissolution in the intergranular pores. As for micropores,
298 decrease of T_2 for the leftmost peak after reaction is observed, indicating
299 the pore size decreases in micropores, because of mineral precipitation. In
300 addition, the porosity fractions of MH3 are calculated from T_2 distributions,
301 as shown in Figure 9 (A). After reaction, the incremental porosity of inter-
302 granular pores increased from 0.987 to 0.989, and the corresponding porosity
303 increased from 19.22% to 19.45%.

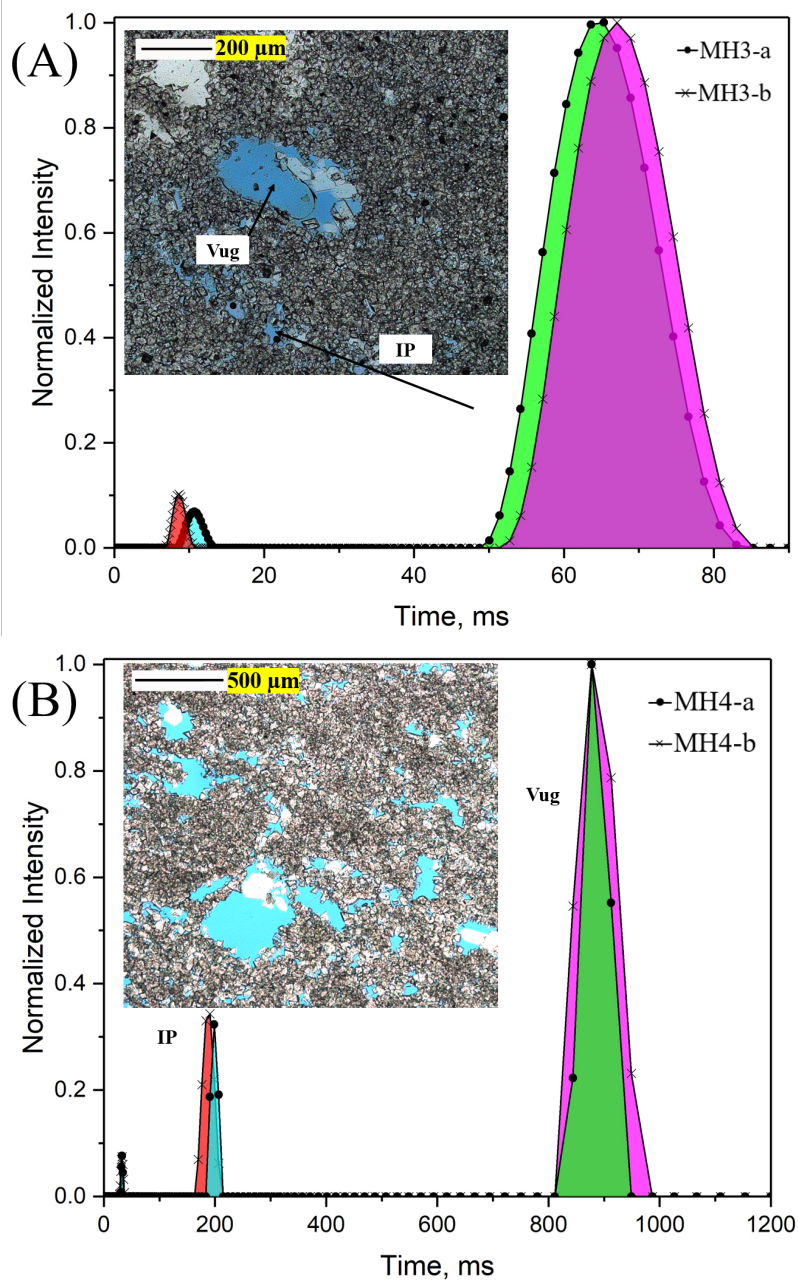


Figure 8: NMR T_2 distributions of MH3 (A) and MH4 (B) prior and post reacting with CO_2 -enriched brine. a: prior reaction; b: after reaction. Thin section images before reaction shown with the T_2 distributions are used to clearly link the peaks to the pores.

304 In contrast with sample MH3, mineral dissolution and precipitation are
 305 complex for vug-dominant porous media, especially for the intergranular
 306 pores. Figure 8 (B) shows three peaks corresponding to micropores, in-
 307 tergranular pores and vugs from left to right for sample MH4. Shifts of the
 308 dominant peak are not recorded for the rightmost peak (vugs) after reaction.
 309 However, the T_2 spectrum of vugs becomes wider because of mineral disso-
 310 lution. Porosity of the vuggy pores calculated from the porosity fractions
 311 (shown in Figure 9 (B)), increased from 14.95% to 15.62%. T_2 representing
 312 intergranular pores after reaction in sample MH4, decreases from 198.5 to
 313 190.1 ms due to mineral precipitation. Similar findings were observed from
 314 pore radii distribution calculated from mercury intrusion capillary pressure
 315 curves. Wang et al. (2020) observed that for micropores ranging from 0.2 to 1
 316 μm , the porosity fraction decreases after reaction due to mineral precipitation
 317 that clogs these pores or their accessibility. For intergranular pores, perme-
 318 ability is controlled by the micropores or small pore throats, their content
 319 is unlikely displaced by CO_2 -enriched brine. Besides, minerals are likely to
 320 dissolve in the intergranular pores that are connected to vugs along the high
 321 permeable pathways. However, these dissolution should not be interpreted
 322 directly and singly from changes in the T_2 peaks position. The evidence of
 323 dissolution can be inferred from the fact that the porosity of the intergranular
 324 pores increased from 1.32% to 1.59%.

325 Pore-size distribution analysis via T_2 distribution together with texture
 326 analysis indicate that the heterogeneity of the pore structure has a signifi-
 327 cant effect on dissolution and precipitation events. Mineral precipitation is
 328 favored in zones of reduced fluid transport, such as micropores for samples

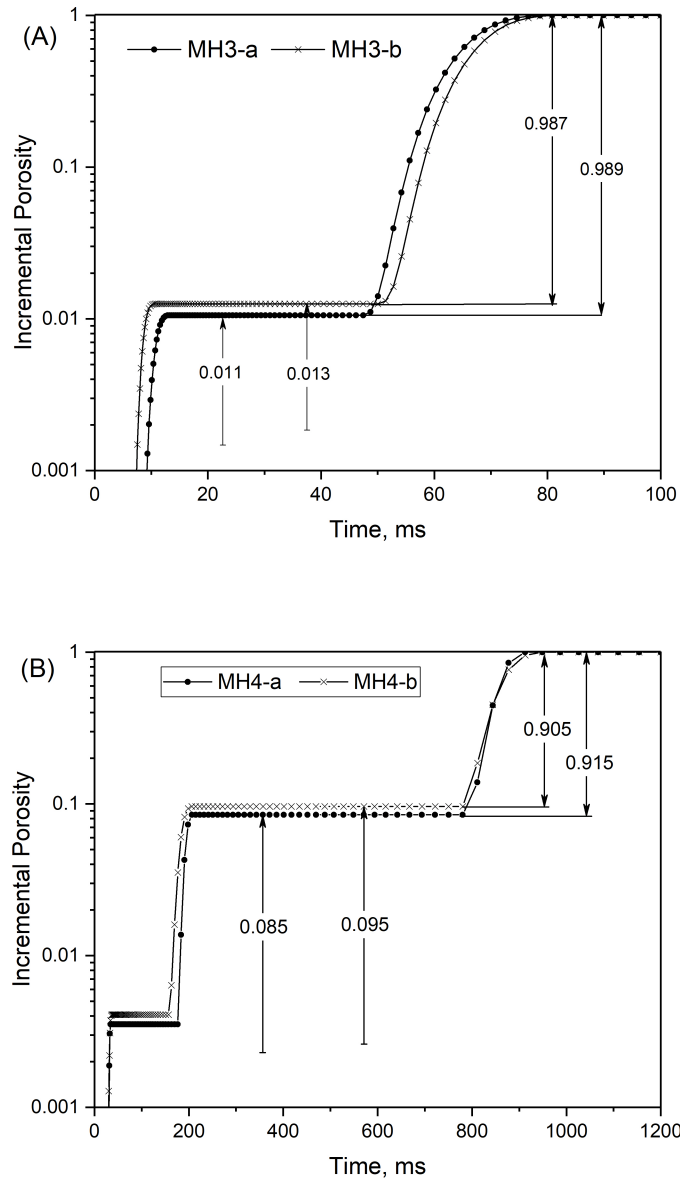


Figure 9: Incremental porosity calculated from T_2 distribution for samples MH3 (A) and MH4 (B) prior and post reacting with CO_2 -enriched brine. Porosity fraction under the peaks from left to right for sample MH3 prior and post reaction are 0.013, 0.987 and 0.011, 0.989, respectively. For sample MH4, porosity fraction under the rightmost peaks decreased from 0.915 to 0.905.

329 MH1 and MH3 and micro/intergranular pores for samples MH2 and MH4,
 330 where chemical gradients are small and likely facilitate localized supersatura-
 331 tion of the fluid and increase of pH (Andreani et al., 2009). In contrast, larger
 332 chemical gradients develop at the mineral/fluid interface in larger pores, in
 333 which molecular transport is more active. In addition, viscosity differences
 334 between CO₂-saturated brine and displaced brine might also favor a hetero-
 335 geneous distribution of reactions. The viscosity of CO₂-saturated brine is less
 336 than that of the displaced brine at reservoir conditions (Duan and Sun, 2003;
 337 Islam and Carlson, 2012; McBride-Wright et al., 2014). CO₂-saturated brine
 338 may preferentially percolate through high permeable pathways, i.e. inter-
 339 granular pore and vugs in samples MH3 and MH4, respectively. Thus, after
 340 brine displacement was stopped, CO₂-enriched brine was located mainly in
 341 larger pores, while the CO₂ concentration of brine in small pores was low
 342 or could be ignored. In diffusion-dominated reactions where carbonic acid
 343 is introduced into the system, dolomite dissolution took place within pore
 344 throats and larger pores. Mineral dissolution may have subsequently en-
 345 larged the size of pore throats and large pores, and increased calcium and
 346 magnesium ion concentrations. Aqueous calcium and magnesium in large
 347 pores might migrate to smaller pores (micropores for MH3 and intergranu-
 348 lar pores for MH4) driven by concentration gradients, which are controlled
 349 by static properties such as pore structure and molecular transport proper-
 350 ties such as diffusion. Within smaller pores, those with poor fluid transport
 351 properties, mineral precipitation becomes dominant because of fluid super
 352 saturation with respect to calcite and dolomite. This precipitation occurs
 353 while minerals dissolve in larger pores with greater potential for fluid flow.

354 In addition, within micropores containing fluid supersaturated with respect
355 to calcite and dolomite, small particles on the surface of dolomite crystals
356 are difficult to dissolve and might serve as effective nucleation sites (Noiriel
357 et al., 2016), thus decreasing the size of smaller pores.

358 3.3. *Effective Diffusion Coefficient Distributions*

359 Molecules and ions diffuse in the restricted pore space representing a com-
360 plex transport mechanism that affects dissolved CO₂ transport as well as the
361 heterogeneous distribution of different reactions under stagnant fluid condi-
362 tions. In contrast with the four core plugs that contact the reactant fluid
363 inside a core-holder, samples MH5 and MH6 were submerged in CO₂-enriched
364 brine. The effective diffusion coefficient of hydrogen-carrying molecules mea-
365 sured by the PFG-NMR method provides information on dynamic transport
366 properties in the restricted pore space.

367 The average diffusion coefficient of water molecules in a pore measured by
368 PFG-NMR is dependent on observation time and surface area-to-pore volume
369 ratio (inversely proportional to pore size). At short observation times, the
370 mean squared displacement for effective diffusion is significantly smaller than
371 the average pore size and only a small fraction of the water molecules can
372 reach the restricting surface. In this study, the observation time is set a con-
373 stant, thus the measured diffusion coefficient is proportional to the average
374 pore size. At the same gradient strength, the effective diffusion coefficient
375 of both samples increased after the reaction process, shown in Figure 10.
376 As temperature and brine chemistry are the same during all measurements,
377 increased effective diffusion coefficient values provide an indicator of the min-
378 eral dissolution (Wang and Alvarado, 2018).

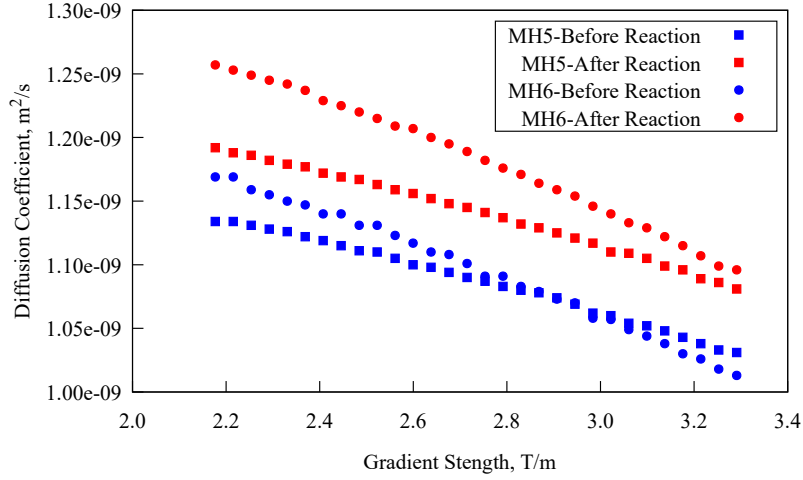


Figure 10: Effective diffusion coefficient decay of samples MH5 and MH6 before and after reaction.

From our previous work, the spatial distribution of the effective diffusion coefficient can be determined by the non-negative least-square method (Wang et al., 2018). Unlike T_2 distributions that are bimodal, the effective diffusion coefficient distribution before reactions for MH5 shows unimodal distributions (Figure 11). The difference in the number of modes is because the pore volume of the mini plugs is small, and the signal from micro pores, where the pore volume is much smaller compared to the pore volume of intergranular pores, is too weak to be captured by the probe. However, a small peak emerged after reaction because of the increase of pore volume in pore throats or micropores due to mineral dissolution. Moreover, the effective diffusion coefficient value at the dominant peak increased because of the increase in the pore size of intergranular pores, which agrees with changes in the T_2 distribution. Sample MH6 yielded two T_2 peaks, which we associated with macro and intergranular pores. The small peak shows that the pore

393 volume of intergranular pores is small compared with macro-pore volume.

394 The spatial distribution of the effective diffusion coefficient for samples
395 MH5 and MH6 provides an indication of heterogeneity of reactive trans-
396 port. Effective diffusion coefficients of cations (like calcium and magnesium)
397 and molecules in macro-pores lead to transport of cations and molecules to
398 micropores as driven by the concentration gradient as well as random trans-
399 lational motion (Stepišnik, 1993). Preferential diffusion likely accelerates
400 mineral precipitation within smaller pores and pore throats between micro
401 and macropores. These smaller pore throats and micropores decrease in size
402 by way of mineral precipitation. However, because of the relatively small
403 pore volume of micropores, an equilibrium might be reached as the concen-
404 tration gradient decreases, which would slow down the diffusion of calcium
405 and magnesium in response to the corresponding mineral precipitation.

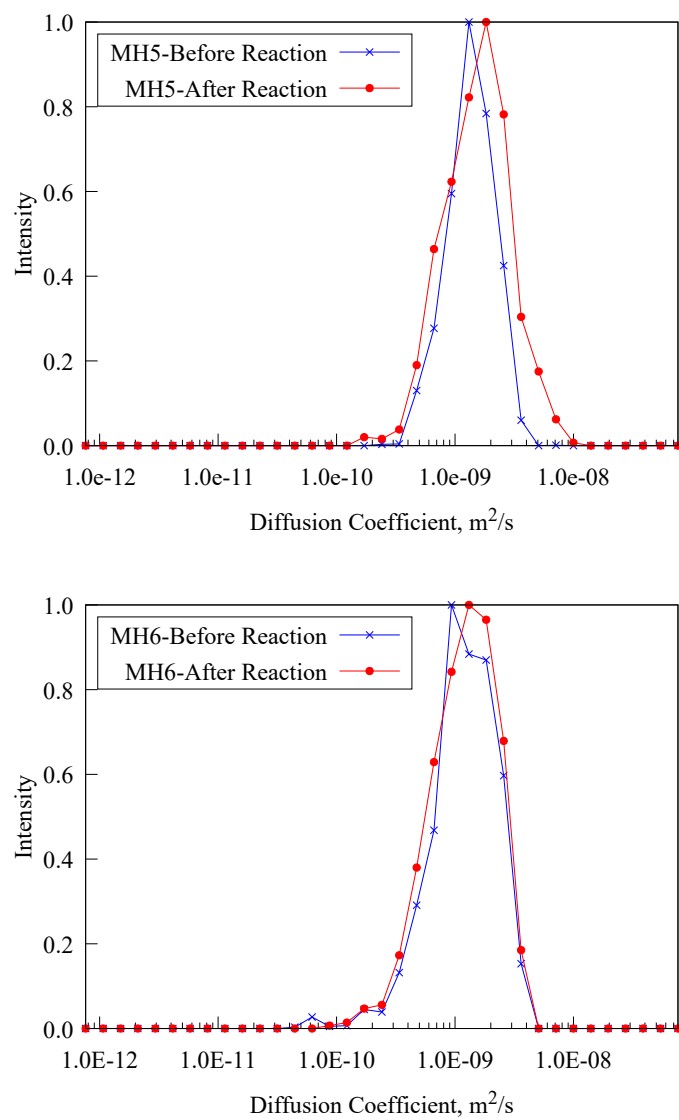


Figure 11: NMR diffusion coefficient distributions of mini plugs before and after reaction under stagnant conditions.

406 4. Conclusions and Implications

407 In this study, we focused on how porosity and permeability respond to
408 pore structure and petrophysical property changes for two rock types, as well
409 as the impact of heterogeneity of mineral dissolution and precipitation during
410 CO₂-enriched brine reaction experiments in the absence of flow. Two types
411 of dolomite samples (intergranular- and vuggy-dominant) were reacted with
412 stagnant CO₂-saturated brine at reservoir conditions (93 °C and 34.5 MPa)
413 for approximately 400 hrs. After stagnant reactions, SEM imaging anal-
414 yses show mineral dissolution in intergranular pores for the intergranular-
415 dominant core sample, and in intergranular and vuggy pores for the vuggy-
416 dominant core sample. As opposed to the reported outcome of continuous
417 injection of CO₂-enriched brine, mineral precipitations were observed in mi-
418 cropore spaces. These observations are further confirmed by the shift of
419 peak values for the different pore types from the T₂ and diffusion coeffi-
420 cient distributions. For MH3, the location of the peak that corresponds to
421 the intergranular pores shifts from 65.3 to 67.1 ms, while for micropores,
422 decrease of T₂ values after reaction is observed. For sample MH4, the T₂
423 peak corresponding to vugs becomes wider after reaction, and T₂ represent-
424 ing intergranular pores after reaction decreases from 198.5 to 190.1 ms due
425 to mineral precipitation. Even though the volume of the reactive carbonic
426 acid is limited as no continuous flow happened, the comprehensive contribu-
427 tions of the heterogeneous reactions are the subtle increase of porosity and
428 permeability.

429 The spatial heterogeneity of mineral dissolution and precipitation as CO₂-
430 enriched brine is introduced has a great effect on pore structure, especially

431 for pore throat size, thus changing rock porosity and permeability, with im-
432 plications for CO₂ plume propagation and storage capacity. For example,
433 the increased permeability favors fluid flow in porous media, which in turn
434 has the ability to increase CO₂ mobility. In contrast, this rock alteration
435 could lower CO₂ sweep efficiency, especially for heterogeneous formations as
436 pore throats increase in high-permeability pathways and decrease in low-
437 permeability pathways. It is important to note that our experimental con-
438 ditions are representative of a significant portion of the pore space in the
439 subsurface, namely that transport will be diffusion-dominant away from fluid
440 sinks or sources, particularly after injection comes to a halt. Thus, exper-
441 imental results in this study provide fundamental understanding on effects
442 of geochemical reactions on alteration of rock physical properties and sub-
443 sequent dynamics of the multiphase flow system. Consequently, a necessary
444 progression of this study should include investigation on how pore structure
445 changes in terms of mineralogy, roughness of pore surfaces and pore throat
446 size by heterogeneous mineral dissolution and precipitation events. The im-
447 portance of this analysis relates to understanding how reactions can affect
448 the dynamic properties associated with CO₂ such as wettability, relative per-
449 meability and capillary pressure. Changes in these crucial properties may
450 in turn affect multi-phase flow that initiates at the pore scale, hysteresis of
451 drainage and imbibition processes, and capillary trapping. This could have
452 a significant influence on the efficiency of capillary pressure trapping, CO₂
453 plume size and storage capacity. During CO₂ EOR projects, the incremental
454 oil recovery may be affected as well.

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