



Research Article

CO₂/Brine/Rock Interactions in the Cedar Keys-Lawson Formation

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Abstract: It has been reported that among the various geologic storage options, deep saline aquifers have the largest estimated capacity for CO₂ storage. Obtaining knowledge of possible artificially geochemically induced changes to the permeability and porosity of host CO₂ storage deposits will enable us to gain insight on long-term reservoir behavior under CO₂ storage conditions.

An experimental study of the interaction of CO₂/brine/rock on saline formations was conducted in a static system under CO₂ storage conditions. Chemical interactions in the Cedar Keys-Lawson Formation carbonate during exposure to CO₂ and brine under sequestration conditions were studied. Samples were exposed to the simulated *in-situ* reaction conditions for one and six months. The samples were exposed to a model brine at 55 °C and CO₂ pressure of 23.8 MPa (3,500 psig). Computed tomography (CT), x-ray diffraction (XRD), scanning electron microscopy (SEM)-energy dispersive x-ray spectroscopy (EDS), brine composition, core porosity, and core permeability analyses were conducted prior to and after the exposure experiments.

Preliminary permeability measurements obtained from the core samples showed changes after they were exposed to CO₂-saturated brine for one and six months. This observation suggests that mineral dissolution and mineral precipitation could occur in the host deposit altering its characteristics for CO₂ storage over time. The 3D images of the pore space clearly illustrate the degree of dissolution that occurred during exposure. It is noted that the dissolution that occurred during the six-month exposure could have enhanced the connectivity between voids. This may contribute the increase of permeability after the CO₂/brine exposure. In addition, the primary minerals comprising the core are dolomite and gypsum. Both minerals could dissolve in the CO₂/brine environment resulting in the increase of permeability after the six-month exposure.

Keywords: CO₂ sequestration; Cedar Keys-Lawson Formation; chemical interaction; permeability; saline aquifer

1. Introduction

Atmospheric CO₂ as well as other greenhouse gases have been considered as the main contributor to global climate change [1]. To alleviate the effect of anthropogenic CO₂ on global climate change, many strategies are under development that can potentially remove CO₂ from the atmosphere. Among these many strategies, carbon capture and storage (CCS) is identified as a key strategy for reducing the contribution of CO₂ from power plants and energy-intensive industries [2]. In particular, CCS technologies could eliminate CO₂ emissions from power

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plants that use fossil fuels by separating CO₂ from plant flue gas, compressing, purifying, and transporting it via pipeline to underground geologic formations for permanent storage. The potential options for CO₂ storage include underground geological formations such as saline aquifers, depleted oil and gas reservoirs, unminable coal seams, hydrate storage, and CO₂ within enhanced geothermal systems [2]. Saline aquifers are recognized as having one of the highest estimated storage CO₂ capacities within underground geological formations [2].

Numerous studies have been conducted to investigate changes in host rock properties when exposed to CO₂ within the Mount Simon formation, the FugureGen site, the Lower Tuscaloosa formation as well as other potential CO₂ storage sites [3–16]. Studies indicated that the nature of these changes depends on the rock composition and the progressive dissolution of CO₂ in the brine that leads to a decrease in pH [3]. As a result, the main expected process involves dissolution of carbonates and eventually silicates, depending on the kinetics of the individual reactions [4]. Specifically, dissolution leads to an increase in porosity and permeability as well as changes in the mineral reactive surface area. Eventually, the increase of cation concentration produced by mineral dissolution can supersaturate the fluids. In this case, precipitation processes are expected which can lead to further changes of porosity and permeability.

Liu *et al.* [6] conducted a simulation study of potential effects of CO₂ sequestration in the Mount Simon sandstone. They reported that a strongly acidified zone (pH 3–5) forms in the areas affected by the injected CO₂ and consequently causes extensive secondary mineral precipitation (calcite, magnesite, ankerite, alunite and anhydrite) and dissolution of feldspars. During the injection period of 100 years, the major chemical reactions are dolomite dissolution and calcite, magnesite, and ankerite precipitation. These carbonate reactions caused a slight increase in porosity (1%). Acidification resulting from CO₂ dissolution eventually caused dissolution of nearly all K-feldspar (21.2% by volume) near the injection well and replacement by alunite and anhydrite. The net permeability change was not reported but was likely to be significant. Szecsody *et al.* [17] conducted a CO₂/brine/rock interaction study with the Mount Simon sandstone and the Eau Claire shale cores obtained from the FutureGen storage site (Jacksonville, Illinois) for a period of 1.2 years at 38 °C and CO₂ pressures up to 12.4 MPa. They reported a significant increase in Mg, K and SO₄²⁻ concentrations, the dissolution of hematite coating on the quartz grains, significant precipitation of NaCl, KCl, and some iron oxide particulate movement. No permeability or porosity changes were measured in this study. Soong *et al.* [18] found that mineral dissolution/precipitation could occur under CO₂ storage conditions for samples obtained from the Mount Simon formation (Indiana). Complementary core-scale numerical simulations of the Mount Simon sandstone/CO₂-saturated brine geochemical interactions predicted dissolution of feldspar and quartz with subsequent formation of kaolinite which would result in a net decrease in core-scale permeability [19]. Tutolo *et al.* [20] conducted studies in K-feldspar rich sandstone from the Eau Claire formation (Indiana) at 150 °C, and 20 MPa using a flow-through apparatus. Results of that study indicated dissolution of feldspar and precipitation of secondary aluminum minerals, such as boehmite. They also reported a decrease in bulk permeability and lower porosity in the post-experiment core samples. It has been reported that the permeability of the reservoir rock is affected by the combination of dissolution and precipitation [18]. Noguez *et al.* [21] also reported that dissolving the small amounts of cementing minerals, such as calcite, can change the permeability significantly.

In addition, Core samples from the Mount Simon formation in Illinois (the FutureGen site) were utilized under CO₂ sequestration conditions of 85 °C and 23.8 MPa of CO₂ in the presence of brine [22]. A 12% decrease in permeability was found in the sandstone cored parallel to the bedding plane after it was exposed to CO₂ saturated brine for six months. This was probably due to mineral dissolution, migration and secondary mineral precipitation altering the sandstone pore/crack structure. For the case of the core sample taken perpendicular to the bedding plane, decreasing permeability may be linked to mineral precipitation in the flow pathway. Furthermore, the measured vertical core permeability is much less than that measured parallel to the bedding plane suggesting CO₂ flow would be more likely parallel to the bedding plane than perpendicular to the bedding plane. This suggests that the tendency of flow to move laterally through the formation (parallel to the bedding plane) rather than up through the formation will only be accentuated by mineral reaction, resulting in potentially greater than expected plume extent and lower reservoir sweep and storage efficiency.

Furthermore, a study to probe the geochemical interactions of the CO₂/brine/rock system under geologic CO₂ storage conditions was conducted in a static reaction system using core samples obtained from the Lower Tuscaloosa formation at the Plant Daniel CO₂ storage test site (Jackson County, Mississippi) [23]. Chemical interactions in a Lower Tuscaloosa sandstone core sample and a Selma chalk core sample were studied under the expected conditions of sequestration in the Lower Tuscaloosa sandstone formation in the presence of CO₂ mixed with brine. The study found a 7% decrease in porosity and the 13% decrease in permeability in the sandstone core after it was exposed to CO₂ saturated brine for six months. The decrease was due to feldspar dissolution, migration and secondary mineral precipitation altering the sandstone pore/crack structure. The low content of active mineral phases in the Lower Tuscaloosa sandstone sample and the high initial porosity of the sample lead to a smaller

permeability change for the sample after 180 days of exposure. For the Selma chalk, the unchanged permeability suggests that the Selma chalk is a good candidate as a secondary seal.

Thus, the injection of CO₂ into a deep saline aquifer affects porosity since it can cause both mineral dissolution and precipitation in the formation. The change of porosity due to mineral reactions may adversely influence the permeability. This permeability change depends not only on the porosity, but also on the details of the pore space geometry and the distribution of precipitates within the pore space. During CO₂ storage in geologic formations, it is expected that supercritical CO₂ will dissolve into the formation's brine. The CO₂-charged brine becomes acidic and can react with minerals in the host deposit leading to dissolution, transport and reprecipitation which could affect the permeability.

One potential CO₂ storage reservoir in Florida is identified within the Lawson and Cedar Keys Formations of the South Florida Basin at a depth of between 900 and 4,000 m. The rocks are composed of porous dolostone sealed by the thick anhydrites of the overlying middle Cedar Keys Formation with an average thickness of 200 m and average porosity of 20 percent. This deposit encompasses an area of about 22,454,000 acres [24]. The stratigraphic column for the South Florida Basin area is illustrated in Figure 1 [24]. Many of the porous interval within the Cedar Keys-Lawson storage reservoir display lateral continuity and have average porosity around 20%. The estimated CO₂ storage capacity for the reservoir is approximately 97 billion tons of CO₂ which suggests the Lawson and Cedar Keys Formations together could potentially support CO₂ sequestration for the large-scale power plants within this area for their entire 40-year lifespan [25]. The Cedar Keys-Lawson injection zone is a saline aquifer located below Tampa Electric at the Big Bend Power Station in Ruskin, Florida. The project was announced in 2010 and has since ended.

Even through the project ended, there is value in studying the CO₂/brine interaction effects on the Cedar Keys-Lawson formation to improve our understanding of CO₂ sequestration in this type of formation. Core samples from the Cedar Keys-Lawson sandstone were placed in CO₂ saturated brines at sequestration temperature and pressure for a period of six months. These samples were studied *via* petrography, x-ray diffraction and scanning electron microscopy to determine the mineralogical, textural, and geochemical changes that resulted from CO₂ exposure. Because the ability to predict how CO₂ will behave in subsurface reservoirs relies on a detailed understanding of the mineralogical, geochemical, and petrophysical properties of reservoir and seal materials on microscopic to macroscopic scales, the knowledge of geochemically induced changes in the porosity and permeability of the Cedar Keys-Lawson sandstone will enhance our capability to predict CO₂ storage capacity and long-term reservoir behavior. Indeed, a recent review by Aminu and colleagues [2] suggested that rock minerals/brine/CO₂ interaction and its impact on storage reservoir quality (porosity and permeability) is a topic warranting further investigation.

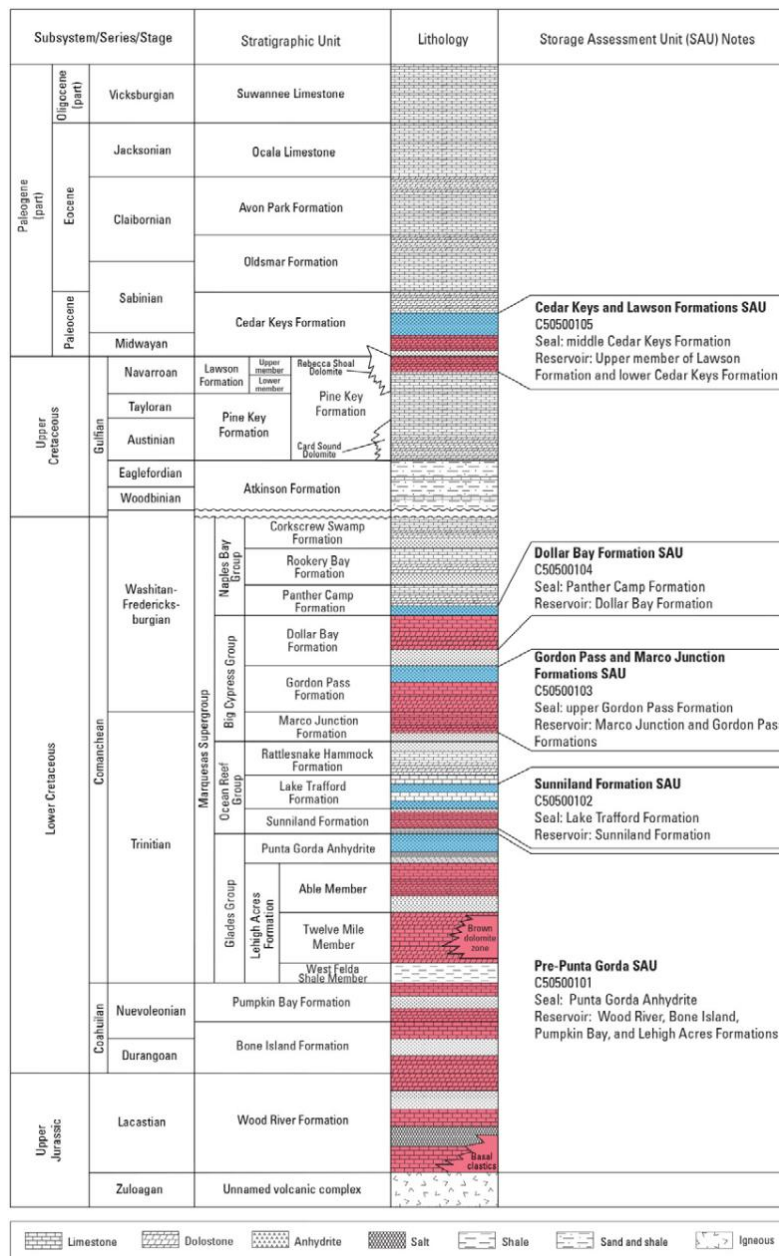


Figure 1. Stratigraphic column for the South Florida Basin study area. Storage assessment units consist of a reservoir (red) and regional seal (blue) [24].

2. Materials and methods

2.1 Core samples and brine

The Cedar Keys-Lawson injection zone is a saline aquifer located below Tampa Electric at the Big Bend Power Station in Ruskin, Florida. The formation is comprised of high porosity carbonates. The Cedar Keys-Lawson cores analyzed here are best described as “a hodge-podge of lithologic features with a dominant limestone signature.

The Cedar Keys-Lawson carbonate samples were obtained from a depth of 1,207 m to 1,208 m from a well located at Polk Power Station in Polk County, Florida. Two core samples approximately 2.54 cm in diameter x 5.08 cm in length were cored parallel to the bedding plan (Table 1). The major mineral composition for the carbonate sample is 90% dolomite, with the balance including anhydrite, gypsum, celestine, quartz, and halite as determined by XRD. Synthetic brine samples were prepared as two liter batches by mixing reagent grade salts of KCl (0.763 g), NaHCO₃ (0.551 g), Na₂CO₃ (0.403 g), NaBr (1.03 g), NH₄Cl (0.593 g), NaCl (202.92 g), MgCl₂·6H₂O (16.729 g), SrCl₂·6 H₂O (3.04 g), Na₂SO₄ (0.083 g), CaCl₂·2H₂O (73.364 g), and FeSO₄·6H₂O (0.956

g) in nitrogen-purged deionized water under constant stirring. Solutions were filtered through 0.45 μm paper filter to remove any particulates prior to use. Mean concentrations from the analysis of dissolved constituents in brine filtrate are listed in Table 2.

Table 1. The change of permeability and porosity of the core interacted with CO₂/brine for one and six months under CO₂ sequestration conditions

	Unreacted Core	Reacted Core	Unreacted Core	Reacted Core
Duration (month)	Fresh	1	Fresh	6
Formation	Cedar Keys-Lawson		Cedar Keys-Lawson	
Obtained				
Depth (m)	1,207		1,207	
Size (cm)	2.54 (O.D.) x 5.08		2.54 (O.D.) x 5.08	
Major ~ 90%	Dolomite		Dolomite	
Minor ~ 10%	Anhydrite, gypsum, celestine, quartz, and halite		Anhydrite, gypsum, celestine, quartz, and halite	
Porosity (%)	19.50 \pm 0.2	19.35 \pm 0.1	24.4 \pm 0.1	24.1 \pm 0.1
Permeability (mD)	4.57 \pm 0.1	4.50 \pm 0.1	44 \pm 1.0	47 \pm 1.0

Table 2. The analysis of synthetic brine and the brine interacted with CO₂/carbonate for one and six months under CO₂ sequestration conditions

	Generic Brine, Batch # 4	Reacted Brine after 1 Month	Generic Brine, Batch # 3	Reacted Brine after 6 Months
	ppm	ppm	ppm	ppm
Ca	12,045	11,793	9,833	11,115
Cu	~	~	0.55	0.85
Fe	521	122	46	~
K	335	395	809	981
Mg	836	988	788	1148
Na	39,695	39,966	38,290	43,332
S	50	68	40	77
Si	~	~	~	10
Sr	462	437	454	265
Chloride	84,347	84,797	72,662	72,478
Bromide	428	428	214	214
Sulfate	284	612	220	455
pH	5.78	5.44	6.02	5.75

2.2 Reactors and experimental procedures

Two 1.8 liter (N4683-T-HC-7500 C276) high-pressure vessels (9.53 cm I.D. by 26.67 cm depth) manufactured by Parr Instrument Company, Erie, Pennsylvania, were used for this study. An open Teflon cell (7.62 cm I.D. x 10.16 cm length) and a smaller Teflon reaction cell insert (6.35 cm I.D. x 9.52 cm length) were used inside the pressure vessels. An ISCO 260D syringe pump was used to charge each vessel with CO₂ and to maintain the pressure in the reactor. Temperatures were maintained within ± 1 °C. A diagram of the reaction system can be found in Figure 2.

In a typical experiment, after loading a smaller Teflon container holding the samples (core and two small chip samples with a volume ratio of brine to core of 5) and brine into a larger Teflon container, the larger container was placed into the pressure vessel. The gap between the two Teflon containers was then filled with brine to ensure that the CO₂ phase was saturated with water vapor without substantially altering the salt concentration in contact with the core sample. The pressure vessel was then purged with CO₂ three times to remove residual air.

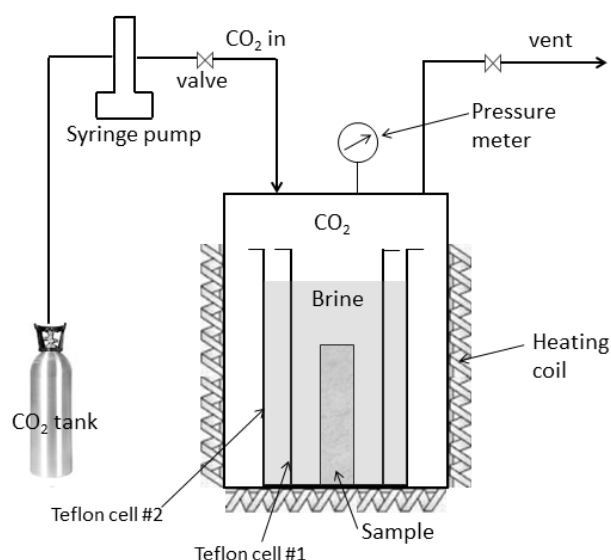


Figure 2. Static reactor system for CO₂-brine-rock study

Finally, the vessel was charged with approximately 4.08 MPa (592 psig) of CO₂ and then slowly heated to a final temperature of 55 °C. During the heating period of about four hours, CO₂ was slowly added to the vessel until the desired testing pressure of 23.8 MPa (3,500 psig) was reached. The two vessels were maintained at these conditions for 1 month (one vessel) and 6 months (second vessel). Upon completion of the experiment, the temperature of the reactor was reduced to room temperature, then the CO₂ was slowly vented and the sample was removed. The solid samples were rinsed with deionized water multiple times to remove residual brine and then dried in a desiccator under flowing N₂. Liquid from the sample-bearing container was recovered for analysis. The reacted brine compositional analysis results are reported in Table 2.

2.3 Analytical methods

2.3.1 Measurements and analysis methods

Before and after the one and six-month tests, the solids were characterized by computed tomography (CT) scanning, x-ray diffraction (XRD), and scanning electron microscopy (SEM)-energy dispersive x-ray spectroscopy (EDS). Inductively coupled plasma-optical emission spectroscopy (ICP-OES) was used to determine metal concentrations in the liquid samples, but due to high salt concentrations, sample dilution with distilled/deionized water was required. Solutions were analyzed for the full range of metals quantifiable by ICP-OES including Al, Si, and Fe. The details of cation and anion analyses, XRD, and SEM-EDS analyses have been reported elsewhere [26].

Porosity and permeability of the samples were measured both before and after exposure. The porosity was measured using a helium porosimeter (HP-401, TEMCO, Inc., Tulsa, OK) at 0.7 MPa at ambient temperature. For both core samples, a TEMCO Ultraperm 500 "flow-through" permeameter and an Autolab 1500 unit from New England Research, Inc. were used to measure the permeabilities [18]. The permeability of the core samples was measured at a confining pressure of 11.63 MPa approximating the depth that the core was collected. Various effective pressures were used to obtain the permeability profile of the core. The porosity and permeability measurements are illustrated in Table 1.

All of the cores were scanned in a Zeiss Versa-X 400 micron CT scanner. Each of the reconstructed pre- and post-images of the 2.54 cm diameter dolomite cores have a voxel resolution between 15.7 and 15.5 μm with 1,440 images. All resolutions utilized were not fine enough to resolve the micro- to nano-scale porosity present in the dolomite. The undetectable pores may connect larger voids that facilitate mass transport. Instrument settings, operating conditions, and scan parameters are described elsewhere [23]. The reconstruction properties of the images were selected to provide the highest fidelity rendition of the scanned sample and to construct a 3-D volumetric representation of the core. The data were exported as a series of 16-bit grayscale cross-sectional TIFF images. Image post processing was performed using the open-source software ImageJ and was reported elsewhere [23].

3. Results and Discussion

To probe the interaction between the cores from the Cedar Keys-Lawson formation and CO₂/brine under CO₂ storage conditions, the following experiments were conducted. The cores were exposed to CO₂/brine at 55°C and 23.8 MPa of CO₂ for one and six months in the static reactors. The porosity measurements conducted on the core sample showed a slight decrease from 19.50% to 19.35% given it is within the measurement errors (Table 1); after it was exposed to CO₂-saturated brine for only one month. The slight decrease of porosity might suggest the precipitation of minerals within the core. Furthermore, the change in porosity was also illustrated in the slight change of permeability (Table 1). The post-exposure permeability of 4.50 mD was reduced slightly from 4.57 mD of the fresh core.

The CT images of the core exposed to CO₂/brine for one month are shown in Figure 3. The pre- and post-exposure samples were scanned in two sections: Top and bottom. The pre-exposure scans were done at 15.7 μm resolution and post-exposure were done at 15.5 μm resolution, each with 1,440 radiographs. The overlap between the top and bottom scans was identified and stitched together to image the entire core. Approximately identical slices from the pre- and post-scans are displayed in Figure 3A and B. No distinguishable differences were present at a macroscopic scale between the fresh and reacted core. The total porosity of the reacted core decreases slightly from 19.5% to 19.35%. However, when viewed in detail, some dissolution was evident around the exterior of the sample. Two locations were identified on the sample exterior, one of which is highlighted by the red rectangle in Figure 3A and B. These areas are shown at higher magnification in Figure 3C and D. Pieces of core were present along the void in the pre-scan image and these particles possibly dissolved during CO₂-exposure. The pore increased in volume by approximately 21% and the equivalent diameter increased from 1,223 μm to 1,304 μm (Table 3).

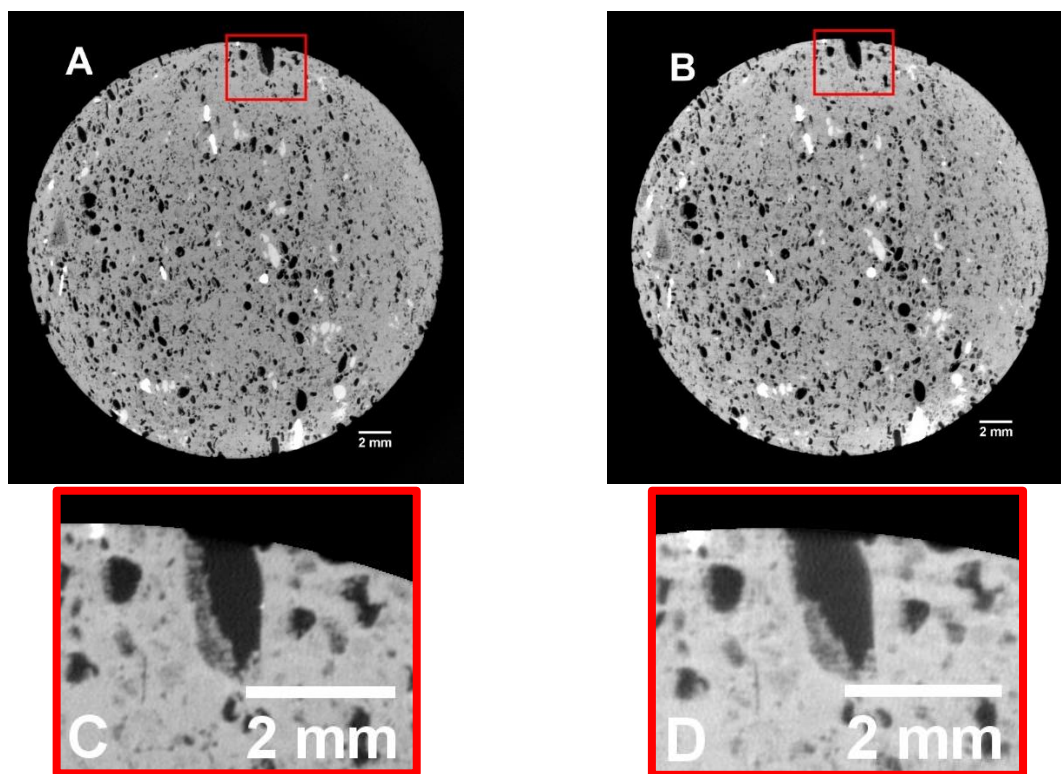


Figure 3. Top: (A) Pre- and (B) Post-exposure highlighted Region of Interest (ROI) in the XY-Plane. Bottom: (C) Pre- and (D) Post-ROI zoomed-in

Table 3. Volume and equivalent diameter changes from Pre- to Post-exposure

	Volume (μm ³)	Eq. Diameter (μm)
Pre-exposure	9.57(10 ⁸)	1,222.67
Post-exposure	1.16(10 ⁹)	1,304.42
Percent Increase	21%	7%

Figure 4 contains 3-D renderings of the pore from Figure 3. Looking at the pore in 3D reveals that the pore both grew in volume and became connected to an adjacent pore by comparing the pre-exposure (4A) to post-exposure (4B) images. The yellow square in Figure 4 highlights an area where the void experienced dissolution (pre-exposure image 4A) either by creating another pore or becoming connected to an adjacent void (post-exposure image 4B).

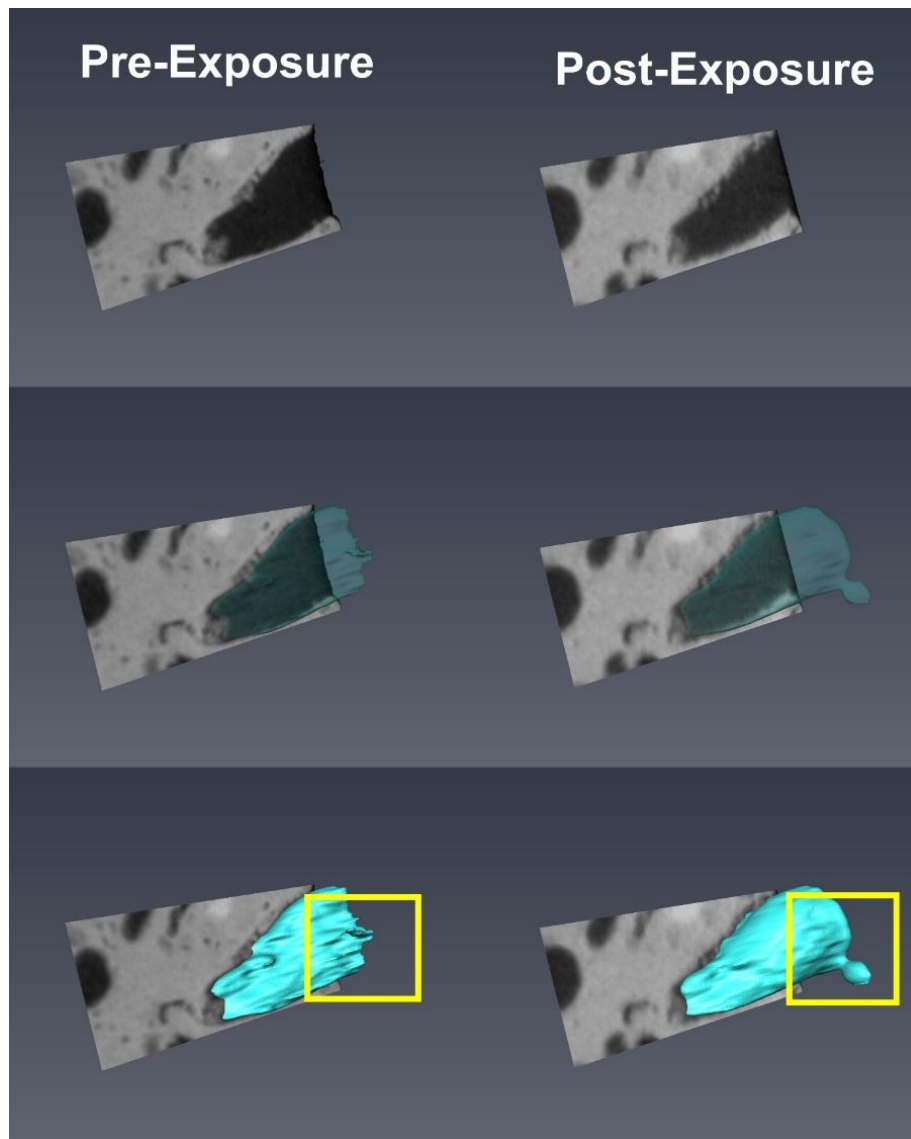


Figure 4. A, Pre- and B, Post-exposure, of 3D renderings of the pore from Figure 3

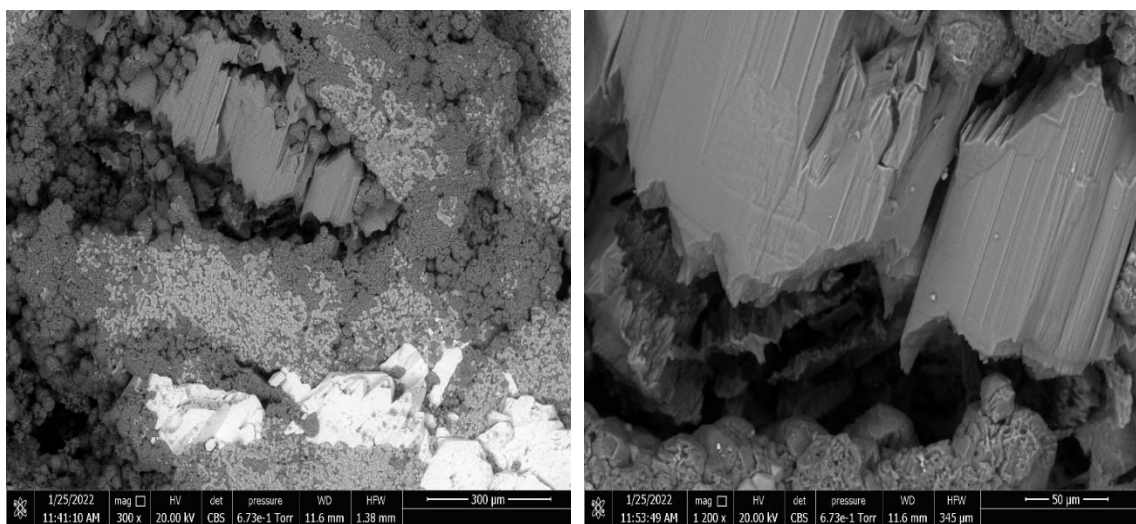


Figure 5A

Figure 5B

Figure 5A and B. The SEM images of sample after exposure to CO₂/brine under CO₂ sequestration conditions for one month. Growth of celestine and dissolution of gypsum/anhydrite was observed

SEM images (Figure 5A, B) were taken after the samples were exposed to the brine and CO₂ for one month. No images were available for these sites prior to exposure, however, based on SEM images for longer exposure times where pre- and post-exposure images were available (see Figure 10), some conclusions can be made. Celestine shows recrystallization or precipitation (Figure 5A) after only one month exposure. This is probably due, at least in part, to the presence of Sr in the brine since the concentration of Sr in the reacted brine decreased (Table 2). The gypsum/anhydrite (Figure 5B) shows evidence of etching/dissolution after one month exposure. This is in accord with the observation from the CT image (Figure 3) that the exterior surface of the core showed some dissolution. Both CT images and SEM images showed the same trend - mineral dissolution occurring after only one month of exposure. Another site (Figure 6A) showed the deposition of a secondary Fe phase on the dolomite, possibly a hydrated Fe oxide, hematite or siderite. At higher magnification (Figure 6B), the secondary Fe phase is more apparent as brighter spots on the dolomite crystal matrix. EDS analysis of this specific site was not conducted. Identification is based on EDS analysis carried out on a similar site, shown in Figure 6C, indicating a high concentration of Fe in the observed particles. This observation of high Fe concentration was also observed for similar morphology particles at other sample sites.

The post-reaction brine was analyzed following contact with the dolomite and CO₂ (Table 2). Comparing the reacted brine with the fresh brine, the following trends were observed. The concentration Fe was decreased. A slight 2% decrease of Ca was also noted, probably within the measurement errors. The concentration of K, Mg, Na, S, Cl, and SO₄⁻ increased after the one-month exposure period. The pH was reduced from 5.7 to 5.44 after the one-month exposure experiment.

Solution chemistry suggested that CO₂-acidified brine may preferentially dissolve gypsum (CaSO₄ · 2(H₂O)) and dolomite (CaMg(CO₃)₂). Thus, an increase in the concentration of sulfate and Mg in the reacted brine were noted (Table 2). The following observations were noted by comparing the solution chemistry before and after exposure to CO₂. The decreasing concentration of Fe may be related to the precipitation of hematite (Fe₂O₃) or another Fe mineral such as siderite (FeCO₃) (Figure 6B). The precipitation of siderite could be due to the interaction between Fe in the solution with dissolved CO₂ in the brine under current experimental conditions. Szecsody *et al.* [17] studied the influence of supercritical CO₂ injection on precipitation, metal migration and changes in the Mount Simon sandstone cores obtained from the FutureGen site in Jacksonville, Illinois (38 °C and up to 12.4 MPa of CO₂ with the presence of brine in the flow through 1-D column). They reported short-term mineral dissolution, ion desorption and iron oxide particulate movement as a result of CO₂ displacement of the brine in larger pores.

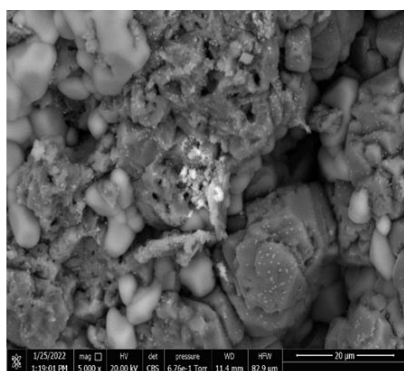


Figure 6A

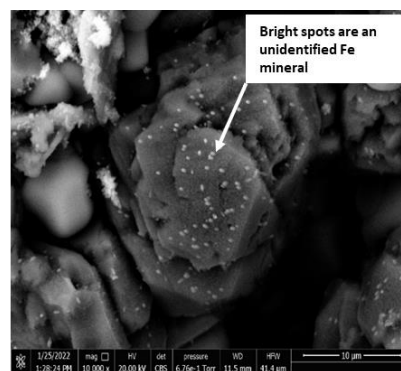


Figure 6B

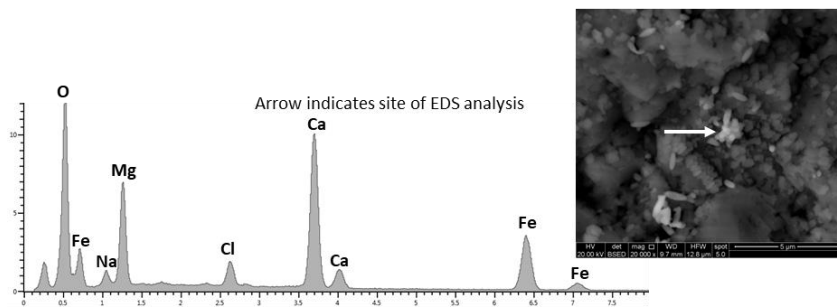


Figure 6C

Figure 6A, B and C. SEM images of samples after exposure to CO₂/brine under CO₂ sequestration conditions for one month. EDS of a similar area to 6B is shown in 6C suggesting that the bright spots on the dolomite crystal are an Fe-containing phase

The six-month exposure experiment exhibited more significant changes. Preliminary porosity measurements obtained from the dolomite samples showed a slight decrease from 24.4% to 24.1% for the core after it was exposed to CO₂-saturated brine for six months (Table 1). The slight decrease of porosity might suggest mineral precipitation within the core. Furthermore, the change in permeability showed a different trend (Table 1) compared to that of one month result. The post-exposure permeability of 47 mD from the core was about 7% higher than the measured pre-reaction permeability of 44 mD in the fresh core. This result suggests that the CO₂/brine exposure alters the pore characteristics by enhancing flow and resulting in permeability increases. It has been reported that the permeability of the reservoir rock is affected by the combination of dissolution and precipitation of minerals such as quartz [18]. Norgues *et al.* [21] reported that even dissolving the small amounts of cementing materials such as calcite, can change the permeability significantly. In addition, the main components of the core are dolomite and gypsum. The dolomite and gypsum may dissolve in the CO₂/brine environment thus resulting in the increase of permeability observed for the six-month exposure sample.

Like the one-month exposure samples, the pre- and post- six-month exposed samples were CT scanned in top and bottom sections and stitched together for analysis. Pre-exposure scans were completed at 15.4 μm resolution and post-exposure were scanned at 15.1 μm resolution each with 1,440 radiographs. Figure 7 displays the same image slice from pre- and post-exposure in the XY-plane. The increase in pore space is prominent along the core diameter from the pre- to post-exposed sample.

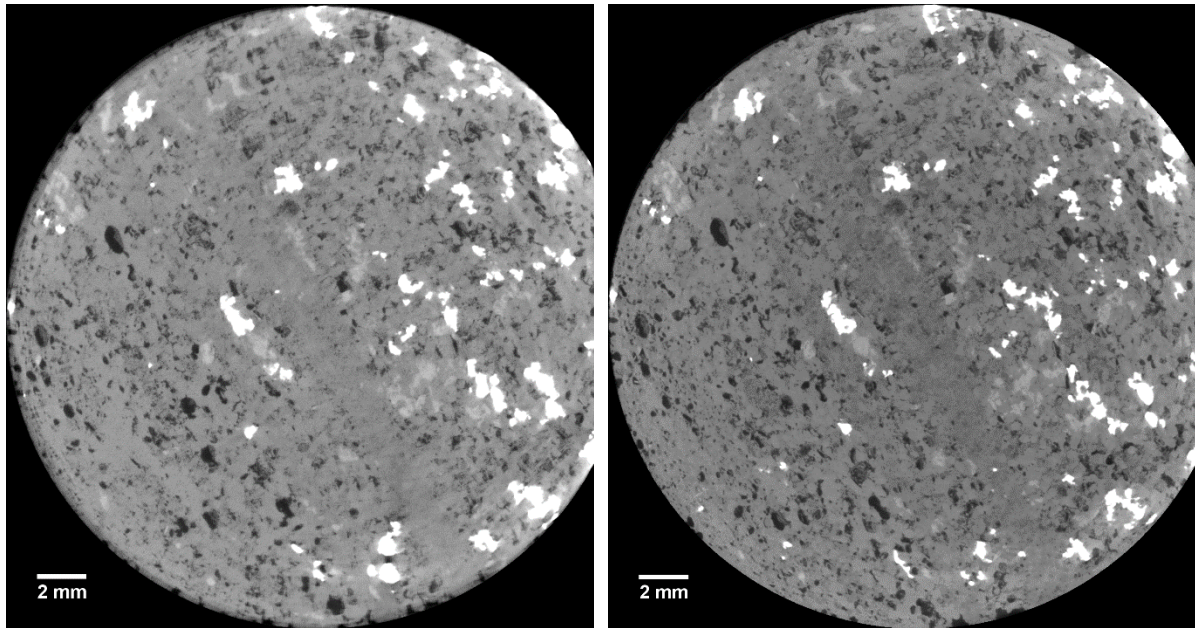


Figure 7. (A) Pre and (B) Post-exposure slice in the XY-Plane

Figure 8 highlights a region of interest in the XY-plane where the pore space adjacent to the core edge increased during CO₂-saturated brine exposure. Slices located above and below the slice shown in Figure 8 were reviewed to verify the alteration in pore space was from exposure and not an artifact of slight changes in scan orientation. The large void present in the post exposure slice (B) highlighted by the red ring was not present prior to exposure (A). Smaller pores also formed within this region of interest. The images in Figure 8C and D are cropped regions from the slices above with the 3D rendering of the surrounding pore space in green. The 3D renderings of the pore space clearly illustrate the degree of dissolution that occurred during exposure (D). It is noted that the dissolution that occurred during the six-month exposure enhanced the connectivity between voids. This may contribute the increase of permeability after the CO₂/brine exposure.

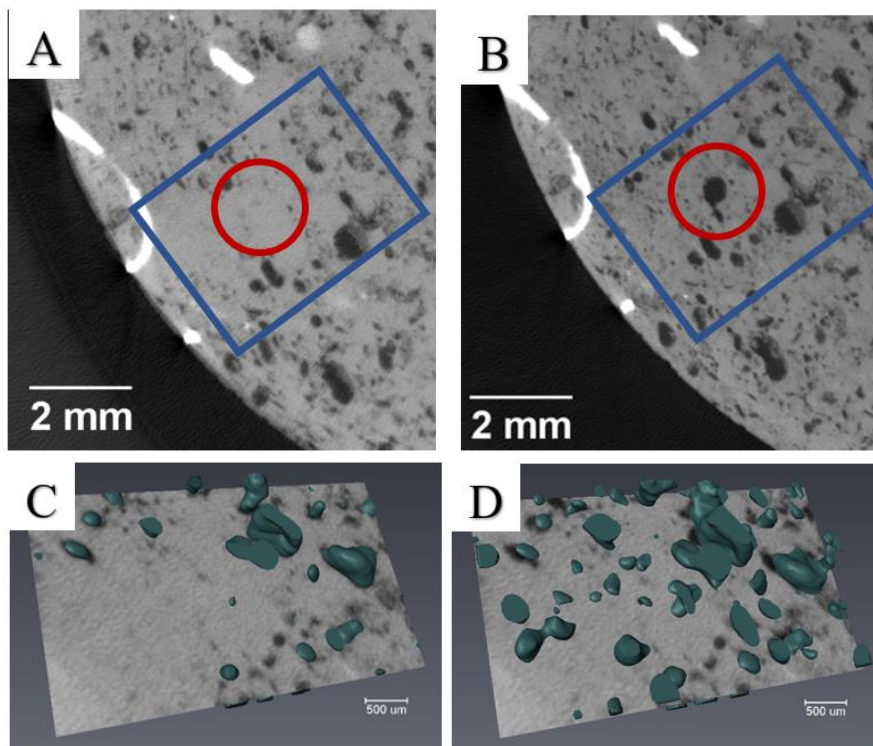


Figure 8. Top: (A) Pre- and (B) Post-exposure region of interest in the XY-Plane; Bottom: cropped corresponding 3D renderings for (C) Pre- and (D) Post- slices

The post-reaction brine was analyzed following contact with the dolomite and CO₂ (Table 2). Comparing the reacted brine with the fresh brine, the following trends were observed. The concentrations of Ca, K, Mg, Na, S, Si, and SO₄⁼ increased. The concentration of Fe decreased after the six months exposure period. The combined information suggests both the dissolution of dolomite and gypsum contribute the observed changes. The pH was reduced from 6.02 to 5.75 after the six months exposure experiment. This observation suggests that mineral dissolution and mineral precipitation could occur in the host deposit altering its characteristics for CO₂ storage over time.

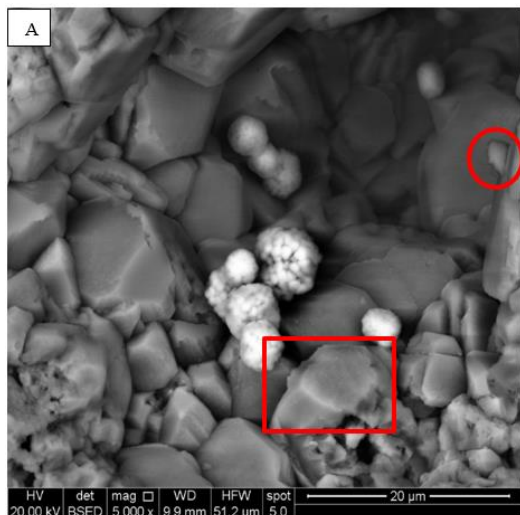


Figure 9A

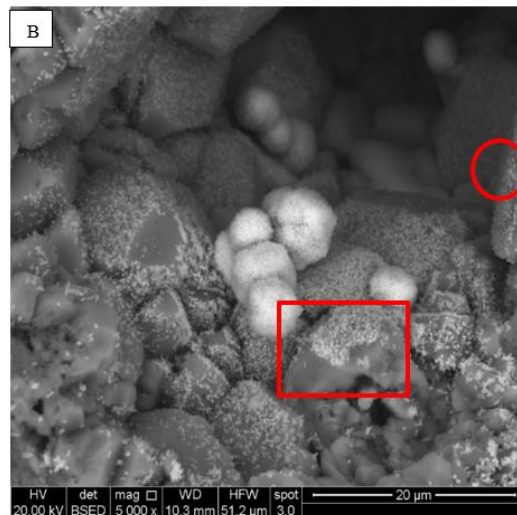


Figure 9B

Figure 9A(fresh) and B(exposed). SEM images of sample before and after exposure to CO₂/brine under CO₂ sequestration conditions for six months

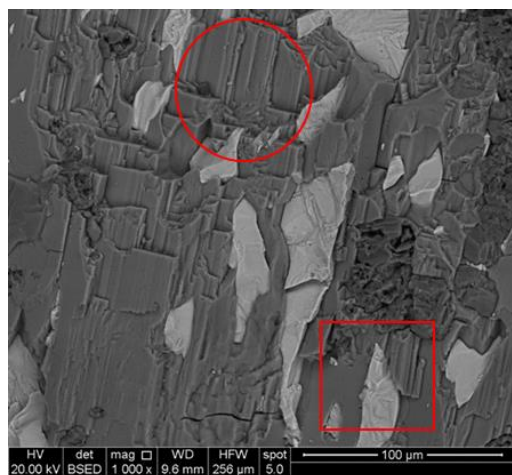


Figure 10A



Figure 10B

Figure 10. SEM images of sample fresh (10A) vs. exposed to CO₂/brine for six months (10B)

The samples were also characterized in detail by SEM before and after exposure to CO₂-brine. SEM analysis results of the core before and after the six-month exposure to the CO₂/brine environment are shown in Figures 9A and 9B.

These figures indicate mineral dissolution as well as mineral growth and precipitation. Figure 9A (fresh) and 9B (exposed) show the backscattered SEM images of the core sample. In the bottom right corner of the before and after images (boxed), evidence of possible mineral precipitation is observed after the six months exposure to CO₂/brine. EDS suggests an iron-containing compound has precipitated on the surface of the dolomite as well as on the pyrite framboid in the center of the image. The iron-containing mineral on and in the vicinity of the pyrite could indicate pyrite has been altered by exposure to the sequestration conditions. In the circled area, mineral dissolution or physical relocation of a mineral particle was clearly observed. This mineral dissolution could result in more flow pathway connections leading to the observed increase in the measured permeability after six months.

This observation is in accord with the finding from CD images (Figure 8). In contrast, in the upper right corner of the image in the circled areas, mineral dissolution was observed after the sample was exposed to CO₂/brine for six months. Figure 10A (fresh) and 10B (exposed) show the backscattered SEM images of the core sample. The circled area in Figure 10A shows a fractured surface of gypsum/anhydrite, identification based on EDS and XRD. The same area in Figure 10B shows that the gypsum/anhydrite has been partially dissolved by exposure to sequestration conditions. The boxed area in Figure 10A shows a fractured celestine surface while the same area in Figure 10B clearly shows the celestine has grown in size with well-formed crystal faces. EDS indicates celestine regrew on fractured, preexisting celestine surfaces. These same results were observed in multiple areas of the sample. The combination of mineral dissolution/mineral precipitation occurring in the sample pores and cracks resulted in a net decrease in porosity as well as enhancing the connectivity between pores leading to the observed 7% increase in permeability.

With only the one- and six-month experimental results obtained and analyzed so far, the host reservoir rock already exhibits a decrease in porosity and an increase in permeability. The results to date are not able to accurately predict the long-term impact on CO₂ sequestration in the Cedar Keys-Lawson Formation but do provide valuable insight. Continuing longer-term exposure experimental work together with computer simulations should provide improved predictions of host rock behavior under CO₂ sequestration conditions. Eventually, reservoir-scale simulations should also aid in understanding the long-term impact on the reservoir rock under CO₂ sequestration conditions. Similar types of studies were reported by Wang et al. [14] and Zhang et al. [16].

4. Conclusions

An experimental study of the interaction of CO₂/brine/rock modelling saline formations was conducted in a static system under CO₂ storage conditions. Core samples from the Cedar Keys-Lawson Formation in Florida were investigated. Chemical interactions of the core carbonate upon exposure to CO₂ and brine under sequestration conditions were studied. Samples were exposed to simulated *in-situ* reaction conditions for one and six-month periods.

In a typical experiment, a core sample with a model brine was reacted under static conditions at 55 °C and a CO₂ pressure of 23.8 MPa (3,500 psig). CT, XRD, SEM-EDS, brine chemistry, porosity, and permeability analyses were conducted prior to and after the experiments.

Preliminary permeability measurements obtained from the core sample showed a change after it was exposed to CO₂-saturated brine for one and six months. This observation suggests that mineral dissolution and mineral precipitation could occur in the host deposit altering its characteristics for CO₂ storage over time. Both SEM and 3D images of the exterior surface as well as pore space clearly illustrate the degree of dissolution that occurred during exposure. Mineral dissolution was observed during the one-month exposure and was found to be more significant after the six-month exposure, likely enhancing the connectivity between the voids. This probably contributed to the change of permeability after the CO₂/brine exposure. In addition, the primary minerals comprising the core are dolomite and gypsum. Both minerals could dissolve in the CO₂/brine environment resulting in the increase of permeability of the six-month exposure.

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Conflict of interest

There is no conflict of interest for this study.

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